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THE VELOCITY OF SAPONIFICATION OF METHYL ACETATE BY SODIUM HYDROXIDE AT 25°

By Wilby T. Gooch and Ethel M. Terry

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As a part of a systematic study of catalysis in homogeneous solution carried out in this Laboratory[1] under the direction of Professor Julius Stieglitz, an exact measurement has been made of the rate of saponification of methyl acetate of about one hundredth molar concentration in aqueous sodium hydroxide solution at 25°.

Experimental Detail

Except for the case of the ester the preparation of materials, the method of measurement, the exclusion of carbon dioxide of the air from contact with reagents, etc., were the same as described elsewhere.]

Methyl acetate was prepared, first, by fractionation of Kahlbaum's best grade of ester, second. by the reaction of acetic anhydride and methyl alcohol and, third, by the reaction of acetic acid and methyl alcohol catalyzed by sulfuric acid as described by Wade2 and purified by the method of Wade and Merriam.[3] All samples were neutral to azolitmin in water solution. No difference was found for the rate of reaction of the ester of these samples.

In this work and in part of the work of Wilson and Terry[4] a special apparatus was used to take the samples of the reaction mixture for analysis at noted times. The apparatus, which was developed jointly with Wilson, will now be described with the assistance of Fig. **1.** The main parts are as follows: **(1)** the flask **A** which held the reaction mixture, **(2)** the valve tube B connecting A with the mercury pipet C from which mercury was discharged into **A,** producing simultaneously the discharge of an equal volume of the reaction mixture from e, the delivery tube of A, into the receiving bottle at M, **(3)** the reservoir E from which mercury was forced into C as it was needed, **(4)** the device **H** by means of which the delivery tube A could be freshly filled with solution just prior to the discharge of mercury from C, and (5) the coiled copper tube F through which water from the hydrant passed into E, thus supplying the pressure

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[1] See ref. **2** of Terry and Stieglitz, This Journal, 49, **2216** (1927), for details of this study. The present paper is based on the thesis of Dr. Gooch, which was presented in **1916.**

[2] Wade, **J.** Chem. *Soc.*, **87, 1656 (1905).**

[3] Wade and Merriam, *ibid.*, **101,2429 (1912).**

[4] Wilson and Terry, This Journal, **50, 1250 (1928).**

which caused the flow of mercury from E whenever Stopcock 1 was opened. The apparatus was contained in a de Khotinsky thermostat, the water level of which is indicated by the horizontal broken line in the diagram.

Although much of the apparatus will be evident from the diagram, the following details and explanations are given to complete the very brief description of the apparatus which space permits. The glass to metal, glass to rubber and the glass to glass seals f at z and z′) were made with de Khotinsky cement. Each unit of the apparatus was equipped with a stopcock used only in filling it. These stopcocks are s and 2, 5, 6, 7 and 8.

The mercury pipet C, which was of 98-cc. capacity, had a small cap f with a two-millimeter hole through the top The cap could be removed when it was necessary to clean C.

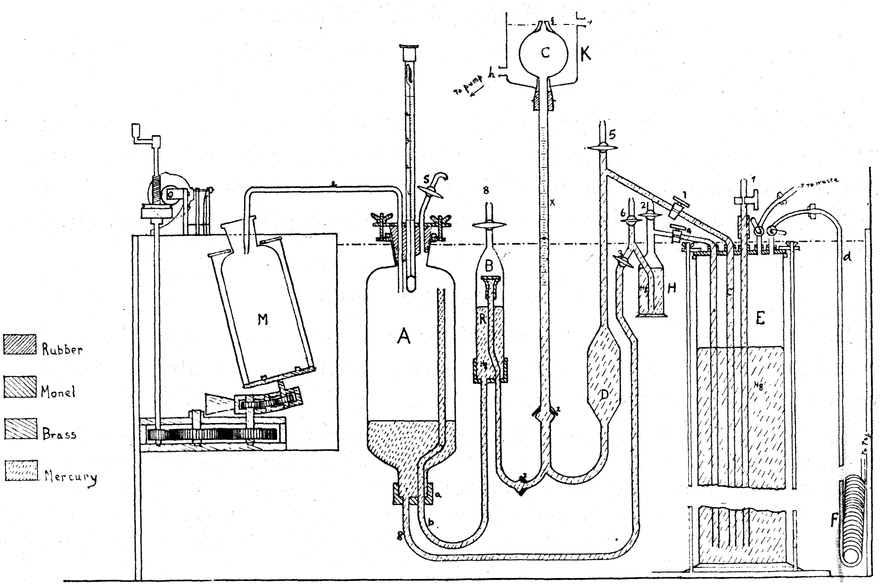

Fig. 1.

Before a bottle had been put in place at M, the operator stopped the exit of e with a finger and opened Stopcock 1. Mercury then flowed upward in C to fill it. Stopcock 1 was then closed and the hole at f was closed with a finger, the operator being careful to leave no air bubble in C. The tip of e was then released and prepared for the discharge of a sample from A in the manner used commonly for pipets. The operator removed his finger from f at the desired instant, thus permitting the entrance of air to C and the discharge of mercury from C through R into the water layer in the top of B. An equal quantity of mercury was simultaneously discharged into A. R was a monel metal cap carrying an adjustable annular slit so narrow that the momentum acquired by the falling mercury in C was expended in forcing the last portion through the aperture into water. With this device the mercury in C descended quietly to a position of rest at a nearly constant level in the graduated stem of C, and a reading was quickly made of the exact location of the meniscus in order to determine the exact volume discharged from A to M. The valve R was designed and made for us by Captain A. de Khotinsky, now of Pentwater, Michigan, who was associated with this Laboratory at the time this work was done.

When an experiment was begun the apparatus had already been filled with mercury to the levels shown in Fig. 1 except in the case of Flask **A,** which was empty. The lugs of the cover of A (see diagram) had been unscrewed and the stopper with its equipment of Beckmann thermometer, discharge tube e and air tube had been removed. After the reaction mixture had been prepared in **A,** the stopper, etc., was clamped in place, mercury was forced into A from E through C and B until all the air was displaced in A, the last bubbles under the stopper being forced out through stopcock s, which was then closed for the remainder of the experiment. The diagram shows the apparatus ready for the first discharge of a measured sample of the reaction mixture.

Constant temperature in C was maintained by means of the water jacket K through which water was pumped from the thermostat in which the main apparatus stood.

The bulb "D" was simply a trap to prevent grease from Stopcock 1 from being carried into C.

The chamber H contained a constant quantity of air under pressure imposed by opening Stopcock 4, thus connecting H with E. When Stopcock 4 was closed and **3** was opened the air compressed in H forced the required amount of mercury into A, thus causing fresh liquid to displace that already in the discharge tube, e. This operation was carried out just before taking a reaction mixture sample. H could be dispensed with when economy of material was not important.

The advantage of the above-described apparatus over that first used in this Laboratory' was that greater ease and speed of operation were possible with it. Only when it was necessary to remove samples every minute was more than one operator needed. Under these conditions two were required instead of three as with the older form.

Another apparatus that simplified work, this time of titration, was the mechanical shaker already referred to. This could be used as shown in Fig. 1 or to shake the samples during titration. The sample taken from the reaction mixture was always discharged into a measured amount of hydrochloric acid sufficient in quantity to more than neutralize the free base present. The titration of the excess acid, which was acetic acid because of double decomposition of hydrochloric acid with sodium acetate, required careful observation of the end-point, as the solutions were dilute. This was made tedious by the necessity of removing mist from the surface of the container, which was at 0° (see ref. 1 for these details).

Captain de Khotinsky, therefore, designed and made for us the shaker in question. It was controlled by a foot switch so that the operator had both hands free for the necessary manipulations. The efficiency of shakers of this type is evinced by the fact that they are still in use (1915–1928) at this Laboratory in cases where the titration samples are large and the observation of the end-point is difficult.

The construction of the shaker, shown at M of Fig. 1, is described briefly as follows. The titration bottle is supported on a circular base and held in place by two rods connected to a semicircular collar that easily slips into place around the neck of the bottle. This circular base is mounted at a slight angle to the horizontal on one end of a counterbalanced frame which is made to whirl by an intermittent electric clutch driven by a small motor (not shown in the diagram). The angle of the base is so adjusted to the height of the bottle that while the base of the bottle is moving in a circle, the opening in its neck does not change its position and thus permits the presence of the buret tip without contact with the neck of the bottle. Thus the frame and the bottle revolve about a perpendicular line (see dotted line at M of Fig. 1) while an equal counter rotation of the bottle itself, produced by a series of compensating gears, prevents the bottle from revolving about its own axis. The advantage of this is that the liquid is whirled within the bottle and not with the bottle. The clutch is made intermittent

because a continuous whirling motion causes the liquid to form layers at the sides of the bottle without mixing with the solution which is being added.

We take pleasure in acknowledging here our indebtedness to Captain de Khotinsky for the design of the valve and shaker.

Results

Coefficients of the rate of the reaction were calculated by means of the following integrated form of the bimolecular reaction equation

$$k = [2.303/(t_2 - t_1)(B - E)] \log (B - X_1)(E - X_2)/(B - X_2)(E - X_1) \quad (1)$$

The initial concentration of ester and base are indicated by the letters B and E, respectively; the concentration of ester or base changed up to the time t is called X; K is the coefficient of the reaction.

In Table I are given the results of a representative experiment. The term $(b-x)$ is the composition of the solution with respect to base in terms of f, the normality of standard acid, which was 0.009917. Obviously $(b-x)f = (B-X)$ but the implied multiplication is not carried out since f would subsequently be canceled when (B—X) is substituted in the above equation. The term (b—e) is the composition of the solution at the end of the reaction in terms of f. Obviously $(E-X) = f[(b-x) - (b-e)] = f(e-x)$, e being the concentration of the ester in terms of f, and $(e-x)$ may be used in place of (E—X) in Equation 1. The value of B given in the table was calculated from the dilution of the stock solution used to make the reaction mixture.

TABLE I

RESULTS OF A REPRESENTATIVE EXPERIMENT

Time	$(b - x)$	Temp., °C.	K	K	K
2.050	0.8552	24.967	(2.050 $= t_1$)	(2.800 $= t_1$)	(3.604 $= t_1$)
2.800	.8135	24.970			
3.604	.7756	24.976			
6.917	.6550	24.986	11.64	11.59	11.63
7.992	.6255	24.988	11.64	11.61	11.64
8.908	.6027	24.990	11.67	11.65	11.68
9.900	.5817	24.995	11.61	11.58	11.60
10.925	.5608	24.994	11.64	11.62	11.64
12.112	.5399	24.994	11.63	11.60	11.62
		Av.	11.641	11.614	11.639

$f = 0.009917$

$B = 0.0094$

$(b - e) = 0.2691$

Av. temperature 24.983'. $K_{25.00} = 11.64$.

In Table II is given a survey of experiments. In Part 1 are given the results for temperature close to 25.00' and in Part 2 are given results at temperatures near 25.20°. From the average of the two series at coefficient of 0.0087 per 0.01' change of temperature was obtained. By means of this all results (except those at 25.20°, Part 2) are corrected to 25.00'.

In Part **3** of the table are the results of experiments done under photographic dark room conditions as described elsewhere.[5] It will be seen that

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[5] Gooch, THIS JOURNAL, 49,2257 (1927).

TABLE II

SUMMARY OF THE RESULTS OF THE FIRST SERIES OF EXPERIMENTS (1915)

B	*E*	Temp. (average). °C.	K	$K_{25.00}$
		Part 1		
0.01000	0.00792	24.979	11.674	11.690
.00994	.00726	24.983	11.631	11.644
.00994	.00789	24.980	11.604	11.621
.01009	.00763	24.980	11.650	11.667
.01009	.00728	25.000	11.677	11.696
.01009	.00749	24.975	11.688	11.710
.01009	.00778	24.974	11.709	11.731
.01009	.00785	24.970	11.689	11.714
.01010	.00785	24 962	11.647	11.684
.01010	.00779	24.994	11.669	11.674
.01010	.00788	24.989	11.610	11.619
.01010	.00760	24.975	11.652	11.674
.01011	.00753	24.988	11.654	11.664
.01011	.00803	24.988	11.664	11.674
.01011	.00815	24.990	11.632	11.644
			Av.	11.674
		Part 2		
0.01001	0.00810	25.190	11.799	
.01011	.00765	25.195	11.874	
.01011	.00788	25.178	11.829	
.01011	.00799	25.186	11.839	
		Part 3 (Experiments under dark room conditions)		
0.01010	0.00780	24.997	11.650	11.650
.01010	.00802	24.987	11.612	11.624
.01010	.00770	24.989	11.664	11.674
			Av.	11.649
		Part 4		
0.02003	0.01747	25.010	11.629	11.620
.02003	.01692	25.009	11.624	11.606
.02003	.01665	25.000	11.644	11.644
.02007	.01488	25.006	11.792	11.697
.02007	.01553	24.988	11.674	11.684
.02007	.01589	25.000	11.642	11.642
			Av.	11.649

as in the case of ethyl acetate diffuse daylight has no effect on the speed of the reaction.

In Part 4 are given the results of experiments with mixtures near to 0.02 molar with respect to sodium hydroxide and 0.016 with respect to ester. The difference between the first series of Part 1 and this series is slight and within the limits of experimental error.

Table III gives the results of experiments carried out one year later than the others. The results will be seen to be in good agreement with the earlier ones.

TABLE III

SUMMARY OF RESULTS OF THE SECOND SERIES OF EXPERIMENTS (1916)

B	E	Tem (average?: °C.	K	$K_{25.00}$
		Part 1		
0.01003	0.00758	25.018	11.765	11.748
.01003	.00741	25.026	11.670	11.678
.01003	.00750	25.020	11.731	11.714
.01000	.00754	25.025	11.724	11.702
			Av.	11.710
		Part 2		
0.02012	0.01621	25.031	11.760	11.733
.02012	.01595	25 048	11.727	11.684
.02012	.01607	25.042	11.669	11.634
.01974	.01602	25.045	11.757	11.717
.01986	.01723	25.090	11.739	11.662
			Av.	11.686

The widest deviation of value of $K_{obs.}$ in a single experiment was 1.63%. The average deviation was 0.93%. The maximum deviation of the mean coefficient of each experiment from the average of all is 0.65%. The expected error in timing and measurements of samples was 0.75%. Therefore it may be stated that the value 11.67 has an error not greater than 1%.

Comparison of Results with the Work of Others.—Although various workers[6] have made measurements on the reaction under consideration, only one experiment, that of Walker,[7] is comparable with the present experiments. Professor Walker used the conductivity method. Although he felt uncertain of the first and last quarter of his experiment and his results varied as much as 3%, still his average coefficient was 11.7, differing from the value obtained in this work by only 0.3%.

Summary

Measurements are reported of the rate of saponification of methyl acetate at 0.008 and 0.016 molarity in aqueous solutions of sodium hydroxide of 0.01 and 0.02 molarity, respectively. The coefficient of the reaction for 25.00° was found to be 11.67 moles per minute with a possible error not greater than 1%. It was demonstrated that diffuse daylight has no effect upon the rate of the reaction.

[6] Reicher, ***Ann.*, 228, 278** (1885), experiments at 9.4°; Bugarsky, *Z. physik. Chem.*, ***8***, 398 (1891), measurements at 19.4°; Volkmann, "Dissertation," Freiburg, i/Br, experiments at 0, 10, 20, 30, 40 and 50°.

[7] Walker, *Proc. Roy. Soc. London*, **78A,** 158 (1906).

Two special pieces of apparatus are described. One is a machine for the rapid measurement of samples of a solution without exposure of the latter to air. The other is a device for shaking a solution while it is being titrated.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF PRINCETON UNIVERSITY]

A NEW QUALITATIVE REAGENT FOR SODIUM

EARLE R. CALEY

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It is generally acknowledged that the usual methods for detecting sodium in qualitative analysis are far from satisfactory. The flame test is much too sensitive in that it fails to show whether sodium is present as an essential constituent or whether it is present in traces as an accidental impurity, while the pyroantimonate test is not sufficiently sensitive in the presence of large amounts of potassium and in other respects is an unsatisfactory reagent.

The possibilities suggested by Streng's[1] discovery of a specific microscopical reagent for sodium have not been generally appreciated. This worker found that a solution containing properly adjusted quantities of uranyl acetate, magnesium acetate and acetic acid formed characteristic crystals of a sodium–magnesium uranyl triple acetate when added to solutions containing sodium ions. Streng also noted that certain other bivalent metals might be substituted for magnesium in this reaction and this observation suggested, in part, the present experimental work.

In 1923 Blanchetière[2] devised a magnesium–uranyl acetate reagent that could be used as a precipitant for sodium in ordinary analysis. Kolthoff[3] improved this reagent and tested its value for qualitative purposes. These results were confirmed by Crepaz.[4] Noyes and Bray[5] also showed the value of Blanchetière's magnesium–uranyl acetate reagent as a confirmatory test for sodium in systematic qualitative analysis. In 1927 Kolthoff[6] described a reagent of the same type in which zinc was substituted for magnesium and found that this was an even more sensitive reagent for sodium.

While the two reagents mentioned above are quite sensitive toward sodium, they possess the disadvantage of giving precipitates with potassium when moderate amounts of this ion are present in the solution tested,

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[1] A. Streng, Z. *wiss. Mikroskop.*, **3**, 129–130 (1886); *Chem. Zentr.*, 17, 488 (1886).

[2] A. Blanchetière, Bull. *soc. chim.*, 33, 807–818 (1923).

[3] I. M. Kolthoff, *Pharm. Weekblad*, 60, 1251–1255 (1923).

[4] E. Crepaz, *Ann. chim. applicata*, 16, 219–224 (1926).

[5] A. A. Noyes and W. C. Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Company, New York, 1927, pp. 258 and 472.

[6] I. M. Kolthoff, *Z. anal. Chem.*, 70, 397–400 (1927).

so that when using gram samples, as is usual in qualitative analysis, these reagents cannot be used safely without effecting a separation of the two elements before applying the test for sodium. It has been found that a cobalt–uranyl acetate reagent of the above type is sufficiently sensitive toward sodium for the ordinary purposes of qualitative testing and yet is less sensitive toward potassium than the reagents containing zinc or magnesium, so that it may be safely used for detecting sodium in the presence of potassium when prepared and applied in the manner described below.

Preparation of Cobalt–Uranyl Acetate Reagent.—It was found that the most suitable manner of preparing the reagent is in two portions as follows.

Solution A		Solution B	
Crystallized uranyl acetate	40 g.	Crystallized cobalt acetate	200 g.
Glacial acetic acid	30 g.	Glacial acetic acid	30 g.
Distilled water to	500 cc.	Distilled water to	500 cc.

Each solution is separately warmed to about 75° until all of the salts are in solution and then the two solutions are mixed at this temperature and allowed to cool to 20°. The vessel containing the mixed reagent is then placed in water at 20°, and held at this temperature for an hour or two until the excess of salts has crystallized out. The reagent is finally filtered through a dry filter into a dry bottle.. The solution thus prepared keeps indefinitely.

Experimental Part

General Technique.—In common with the triple acetates containing magnesium and zinc, the triple acetate containing sodium, cobalt and uranyl exhibits a marked tendency to form supersaturated solutions. This tendency is readily overcome by shaking the reagent vigorously with the test solution used. For qualitative purposes it was found that the most satisfactory procedure was to mix the reagent and the solution to be tested in a test-tube and then to stopper the tube and shake vigorously for two to three minutes, finally setting aside for five minutes before making the observation. In the following experiments, standard solutions of pure salts were prepared and tested in this manner. The precipitates formed with this reagent are best observed by holding the test-tube above the level of the eye and then looking at the bottom of the tube, by which means the heavy yellow precipitate that settles to the bottom of the tube may readily be seen in contrast to the deep red reagent.

Reactions of Cobalt–Uranyl Acetate Reagent with Pure Sodium Chloride Solutions.—Table I shows the results of a series of experiments made on solutions of pure sodium chloride.

It will be seen that two milligrams of sodium give an immediate precipitate with the reagent, while one milligram may, with certainty, be detected by allowing the mixture of reagent and sodium solution to stand for an hour or two. The results also indicate the necessity of keeping the volume of sodium solution down to a minimum so as not to dilute the reagent unduly and lead to the non-separation of the triple acetate.

TABLE I

REACTIONS OF COBALT–URANYL ACETATE REAGENT WITH PURE SODIUM CHLORIDE SOLUTIONS

Reagent, cc.	Sodium soln., cc.	Sodium present, g.	Ppt. after shaking and standing for 5 min.	Ppt. after one hour
10	1	0.0020	Marked	Heavy
10	2	.0020	None	Slight
20	1	.0030	Heavy	Heavy
20	1	.0020	Marked	Heavy
20	2	0020	None	None
20	1	.0015	Slight	Marked[a]
20	1	.0010	None	Slight[b]
20	1	.0005	None	None[c]

[a] Marked ppt. in ten minutes. [b] Marked ppt. after several hours. [c] No ppt. in 24 hours.

The reason for using relatively large volumes of reagent appears under the experiments on potassium solutions.

Reactions with Potassium Chloride Solutions.—Table II shows the results obtained in a similar series of experiments in which one cc. of potassium solution was used in each case.

TABLE II

REACTIONS OF COBALT–URANYL ACETATE WITH POTASSIUM CHLORIDE SOLUTIONS

Reagent, cc.	Potassium present, g.	Ppt. after 5 min.	Ppt. after 1 hour	Ppt. after 24 hours
5	0.0500	None	None	....
5	.1000	Heavy	Heavy	....
10	.0500	None	None	....
10	.1000	None	None	Slight
10	.1500	Heavy	Heavy	....
20	.1000	None	None	None
20	.1500	None	None	Slight
20	Sat. KCl soln.	None	Slight	Heavy
20	Sat. K_2SO_4 soln.	None	None	None
10	Sat. K_2SO_4 soln.	None	None	....

It is evident from these results that the use of sufficiently large volumes of reagent favors the non-precipitation of the triple acetate of potassium, cobalt and uranyl. Evidently the concentration of potassium in the total volume of reagent plus solution governs the amount of precipitation and not the concentration of potassium in the original test solution. These experiments showed that a saturated solution of potassium sulfate gives no precipitate with 20 cc. of this reagent and that even a saturated solution of potassium chloride gives no immediate reaction.

Experiments on Precipitating Sodium in the Presence of Potassium.—To determine whether or not the presence of potassium would reduce the sensitivity of the reagent toward sodium, pure sodium and potassium chloride solutions were mixed, evaporated until their total volume was reduced to 1 cc. and then tested with 20 cc. of the reagent in the usual manner. Table III shows the results.

TABLE III

DETECTION OF SODIUM IN THE PRESENCE OF POTASSIUM WITH COBALT–URANYL ACETATE REAGENT

Sodium present, g.	Potassium present. g.	Ppt. after shaking and standing for 5 min.	Ppt. after 15 min.
0.0010	0.0500	Slight	Fair
.0010	.1000	Slight	Fair
.0010	.1500	Slight	Fair
.0020	.1000	Fair	Good
.0030	.1000	Heavy	Heavy

It was therefore concluded that the presence of potassium does not decrease the sensitivity of the reagent toward sodium. If anything, the presence of potassium appears to tend to increase the rapidity of the formation of the sodium–cobalt uranyl triple acetate.

Reaction of Cobalt–Uranyl Acetate Reagent with Various **Ions.**—Solutions of salts of lithium, ammonium, magnesium, calcium, barium and strontium, known to be free from all but traces of sodium, were also tested with the reagent. It was found that the reagent gave no reaction with these ions with the exception of lithium. Even in the case of lithium it is much less sensitive than the corresponding reagents containing zinc and magnesium since 10 mg. of lithium in 1 cc. of solution gave no precipitate and even 20 mg. gave only a faint precipitate after standing for several hours. For the usual student courses in qualitative analysis, the behavior toward lithium is, of course, of no significance. It has been found that most heavy metals give no reaction with this reagent. Phosphates and other anions that would precipitate the metallic constituents of the reagent must be absent, a condition that is automatically provided for in systematic qualitative analysis.

Quantitative Possibilities of this Reagent.—Several experiments were also directed toward determining the possibility of using this reagent for the quantitative determination of sodium, but it is apparently not suited to this purpose. Several analyses of the triple acetate precipitates obtained by this reagent showed that they approximate the composition represented by the formula $3UO_2(C_2H_3O_2)_2 \cdot Co(C_2H_3O_2)_2 \cdot NaC_2H_3O_2 \cdot 6H_2O$. It was found, however, that they tend to vary in composition so much that they are worthless for quantitative purposes.

Application to the Usual Scheme for Qualitative Analysis.—In applying this reagent to the usual plan for the qualitative analysis of the common metals it is preferable to precipitate magnesium along with barium, calcium and strontium according to the well-known procedure of Noyes.[7]

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[7] A. A. Noyes, "Qualitative Chemical Analysis," The Macmillan Company, **1920,** 8th ed.

The filtrate resulting from the ammonium carbonate group may then be treated as follows.

MODIFIED PROCEDURE FOR THE ALKALI GROUP

Acidify the filtrate from Group IV with dilute sulfuric acid and evaporate carefully to dryness in a porcelain dish, finally heating to expel ammonium salts. After cooling treat the residue with 2 cc. of cold distilled water and stir for several minutes to bring the sulfates into solution. Finally filter through a small filter. Divide the filtrate into two equal parts.

Part I.—Test for potassium in the usual way with sodium cobaltinitrite, confirming by means of the flame test.

Part II.—Add **10–20** cc. of cobalt–uranyl acetate reagent, stopper the test-tube and shake thoroughly for two to three minutes. Allow the mixture to stand for at least five minutes. The formation of a yellow precipitate indicates the presence of sodium.

NOTES ON THE PROCEDURE

1. In case large amounts of these alkalies are present the sulfate residue will not all go into solution. This is no disadvantage since the usual tests will be obtained.

2. Care must be taken to use not more than 1 cc. of solution for the sodium test.

3. The amount and speed of formation of the triple acetate precipitate in the test for sodium afford a valuable indication of the probable amount present.

Summary

1. There has been described a new qualitative reagent for sodium composed of a solution of uranyl and cobalt acetates in normal acetic acid.

2. The application of this reagent in the qualitative scheme for the common metals has been indicated.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. V. A REVISION OF THE ENTROPIES AND FREE ENERGIES OF NINETEEN ORGANIC COMPOUNDS

BY GEORGE S. PARKS, KENNETH K. KELLEY AND HUGH M. HUFFMAN

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In four preceding papers[1] the entropies and free energies of eighteen organic compounds have been calculated from heat capacity data by means of the third law of thermodynamics. In these calculations the entropy increase for each compound between zero absolute and 90°K. was obtained by use of the "n formula" of Lewis and Gibson,[2] as in most cases the heat capacity data did not go much below the latter temperature. This formula was recognized as being only a rough first approximation but its simplicity and ease of application justified its use for comparative purposes.

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[1] Parks, THIS JOURNAL, **47,** *338* (1925); Parks and Kelley, *ibid.,* **47, 2094 (1925);** Parks and Anderson, *ibid.,* 48, **1506 (1926);** Parks and Huffman, *ibid.,* 48, ***2788*** **(1926).**

[2] Lewis and Gibson, *ibid.,* **39,2565 (1917).**

However, recent measurements down to liquid hydrogen temperature's, made on a number of these substances by one of us (K. K. K.) at the University of California, have demonstrated that in the case of organic compounds the "n formula" gives results for the entropies at 90°K. which are 20 to 30% too high. Since our entropy and free energy calculations were primarily for comparative purposes, this fact does not invalidate the important conclusions drawn in the preceding papers. However, the desirability of now putting the results on an absolute basis has rendered necessary a revision of our earlier values.

In the case of at least twelve organic compounds heat capacity data for the crystalline state are at present available down to or below 20°K. With the aid of these data we have developed a simple, accurate method for estimating the entropy increases for organic substances between 0 and 90°K. The molecular heat capacity curves for the twelve compounds[3] fall naturally into two classes—one for aliphatic and one for cyclic compounds. In each class the various experimental curves are essentially similar in character and we have been able to construct a type or standard curve. For any particular substance in either class the molal heat capacity at each temperature is given quite accurately by the equation

$$C_p \text{ (per mole)} = (A + BT)C_p^\circ \qquad (1)$$

where A and B are characteristic constants for each substance and C_p° refers to the heat capacity on the standard curve at the temperature T. It then follows that

$$S_{90} = AS_{90}^0 + B\int_0^{90} C_p^\circ \, \mathrm{d}T \qquad (2)$$

where S_{90} is the molal entropy of the substance at 90°K. and S_{90}° is that for the standard. To evaluate A and B it is merely necessary to know C_p for the substance at two different temperatures, 90 and 120°K. for instance, whereupon two independent equations, similar to (1) and involving these constants as unknowns, may be set up and solved. Applying this method to the twelve compounds referred to, we have calculated the respective values of S_{90} and have compared these with the corresponding experimental ones. The average difference is 0.3 E. U., or about 2.6%, and is probably not much greater than the average error in the experimental values.

By means of this extrapolation method we have revised the entropies of the eighteen aliphatic compounds studied in the four preceding papers.

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[3] We are here using the data of Lange, *Z. physik. Chem.*, 110,350 (1924), for quinone and hydroquinol, the results of Simon, *Ann. Physik*, 68, 258 (1922), for glucose, and those of Gibson and Giauque, THIS JOURNAL, 45, 93 (1923), and of Simon and Lange, *Z. Physik*, **38**, 227 (1926), for glycerol. The data for the remaining eight compounds (methyl alcohol, ethyl alcohol, n-hexyl alcohol, *iso*propyl alcohol, acetone, toluene, m-xylene and cyclohexanol) were obtained by the second author in recent work at the University of California.

The new values are given in Table I. For purposes of completeness we have also included formic acid, which was studied by Gibson, Latimer and Parks[4] in a still earlier investigation. In Col. 2 appear the entropy increments from 0 to 90°K., calculated by Equation 2. The third column then contains the entropy increments from 90 to 298°K., as calculated previously from the heat capacity data.

TABLE I

THE REVISED MOLAL ENTROPIES OF NINETEEN ORGANIC COMPOUNDS

Substance	Entropy increment 0–90°K.	Entropy increment 90–298°K.	S_{298}
Methyl alcohol	8.2	22.82	31.0
Ethyl alcohol	9.3	29.13	38.4
n-Propyl alcohol	10.4	35.69	46.1
Isopropyl alcohol	10.2	32.91	43.1
n-Butyl alcohol	11.9	42.56	54.5
Tert.-butyl alcohol	10.8	34.47	45.3
Ethylene glycol	8.5	31.39	39.9
Glycerol	9.9	39.82	49.7
Erythritol	10.6	29.25	39.8
Mannitol	15.3	41.68	57.0
Dulcitol	14.4	41.64	56.0
Formic acid	7.1	23.59	30.7
Acetic acid	10.2	27.98	38.2
Butyric acid	12.8	41.30	54.1
Palmitic acid	35.0	78.66	113.7
Oxalic acid	9.2	19.50	28.7
Ethyl ether	14.0	46.45	60.4
Acetone	12.9	34.93	47.8
Glucose	13.2	37.54	50.5

The entropies at 298°K. appear in the last column of the table; they are probably accurate to within 1 or 2% in all cases. As compared with the results previously published, the present values represent corrections varying from 1.7 E. U. in the case of oxalic acid to 16.2 E. U. for palmitic acid. However, the general principle that the entropy of an organic compound changes in a definite, additive manner with changes in its constitution still holds true. Thus in the normal alcohol series the average entropy increase per CH_2 increment is 7.8 E. U. in going from methyl to n-butyl alcohol. Likewise in the fatty acid series the change from formic acid to liquid palmitic acid at 25° is accompanied by an entropy increase of 120.4 or an average of 8.0 E. U. per CH_2 group.

Employing these revised entropy values, we have also recalculated the free energies of formation of the nineteen compounds by means of the thermodynamic equation $\Delta F = \Delta H - T\Delta S$. The essential data appear in Table II. For obtaining the figures (Col. **3**) for the ΔH_{298} of formation

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[4] Gibson, Latimer and Parks, THIS JOURNAL, 42, 1540 (1920).

of these organic substances, we have used the heats of combustion[5] given in the preceding column in conjunction with the values 68,320 cal.[6] and 94,270 cal.[7] for the heats of combustion at 25° of hydrogen and graphitic carbon, respectively. Column 4 contains the entropy of formation of each compound, which is simply the difference between its S_{298} and the corresponding values for the entropies of the elements contained therein. For this purpose the respective entropies of carbon, hydrogen and oxygen were taken as 1.3,[8] 14.8[9] and 24.5[10] E. U. per gram atom. The resulting

TABLE II

THERMAL DATA AT 298° K.

The 15° calorie is used throughout and all weights have been reduced to a vacuum basis

Substance	Ht. of comb. at const. press., cal.	ΔH_{298}, cal.	ΔS_{298}, entropy units	ΔF_{298}, cal.
Methyl alcohol	170,600	− 60,300	− 54.0	− 44,200
Ethyl alcohol	327,200	− 66,300	− 77.5	− 43,200
n-Propyl alcohol	482,800	− 73,300	−100.7	− 43,300
Isopropyl alcohol	477,100	− 79,000	−103.7	− 48,100
n-Butyl alcohol	638,700	− 80,000	−123.2	− 43,200
Tert.-butyl alcohol	629,100	− 89,600	−132.4	− 50,100
Ethylene glycol	281,800	−111,700	−100.5	− 81,800
Glycerol	397,000	−159,300	−146.1	−115,700
Erythritol	503,700	−215,000	−211.4	−152,000
Mannitol	727,000	−317,000	−305.0	−226,100
Dulcitol	726,000	−318,000	−306.0	−226,800
Formic acid	62,700	− 99,900	− 49.2	− 85,200
Acetic acid	208,100	−117,000	− 72.6	− 95,400
n-Butyric acid	520,000	−130,400	−118.5	− 95,100
Palmitic acid	2,379,000	−222,000	−429.0	− 94,000
Oxalic acid	60,100	−196,800	−101.5	−166,500
Ethyl ether	651,400	− 67,300	−117.3	− 32,300
Acetone	430,500	− 57,300	− 69.4	− 36,600
Glucose	673,000	−303,000	−281.9	−219,000

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[5] For the four alcohols, methyl, ethyl, n-propyl and n-butyl, we have utilized substantially the results of Richards and Davis as recently revised by Swietoslawski and Bobinska, THIS JOURNAL, **49**, 2478 (1927). For isopropyl alcohol and acetone we have used the values calculated by Kelley, THIS JOURNAL, 51, 1149 (1929). In the case of the remaining compounds we have employed the data which will appear in "The International Critical Tables" (private communication from Dr. M. S. Kharasch). In all instances the heats of combustion have been calculated to 25° for our present purpose.

[6] The value selected for "The International Critical Tables" is 68,380 cal. at 18° (private communication from Dr. F. R. Bichowsky); this is equivalent to 68,323 cal. at 25°.

[7] Roth and Naeser, *Z. Elektrochem.,* **31,** 461 (1925).

[8] Lewis and Gibson, THIS JOURNAL, **39,** 2581 (1917).

[9] Giauque and Wiebe, *ibid.,* 50, 121 (1928).

[10] Giauque and Johnston, personal communication.

free energies appear in the last column of the table. The differences between these results and those which were given in the preceding papers vary from 100 cal. in the cases of mannitol and glucose to 5000 cal. for palmitic acid. The accuracy of these revised values is now almost entirely limited by the accuracy of the heats of combustion involved.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE KINETICS OF THE OXIDATION OF IODIDE ION BY ACID DICHROMATE SOLUTIONS IN PRESENCE OF A NEUTRAL SALT

BY RALPH F. BEARD[1] AND NELSON W. TAYLOR

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Introduction

Many ionic reactions show kinetic anomalies in the sense that the order of reaction does not come out an integral number. BrGnsted[2] has made the suggestion that if sufficient neutral salt be added to fix the activity coefficients of the ions, such reactions can be rendered normal.

The oxidation of iodide ion by means of potassium dichromate in acid solution is a reaction of this type.

DeLury[3] and also Kernot and Pietrofesa[4] concluded from their work that the reaction was first order with respect to $Cr_2O_7^{--}$ ion, nearly second order with respect to H^+ ion and between first and second with respect to I^- ion. In the preliminary work of this investigation the data confirmed the results of the above-named workers, but the order of reaction with respect to I^- ion was found to be more nearly second than first. Thus the reaction considered as a whole appeared to be approximately a fifth order one.

The purpose of this work is to test Bronsted's prediction regarding the effect of neutral salt on the kinetics of the reaction and, if possible, to obtain experimental evidence bearing on the activity rate theory of reaction mechanism.

Outline of Experimental Work

A preliminary investigation was made over a wide range of salt concentration. The salt used was sodium chloride and the source of H^+ ion was perchloric acid. Sixteen reaction mixtures were made up with the concen-

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[1] Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Minnesota, June, 1928.

[2] Bronsted, "The Theory of Velocity of Ionic Reactions," Columbia University Press, New York, 1927, p. 13.

[3] DeLury, J. *Phys. Chem.*, 7,239 (1903).

[4] Kernot and Pietrofesa, Rend. *accad. sci. fis. mat. Napoli, IIIA,* 275 (1911).

tration of sodium chloride as shown in Table I. The intial concentrations of the reactants were the same in all determinations and were as follows: $K_2Cr_2O_7$, 2.02 X 10^{-4} *M;* KI, 142 X 10^{-4} *M;* $HClO_4$, 364 X 10^{-4} *M.*

The reaction time was twenty minutes in each case, the extent of reaction being determined by titration with *N*/100 sodium thiosulfate, using starch solution as the indicator. All the solutions except the potassium iodide were mixed in a 250-cc. Erlenmeyer flask. The iodide was placed in a similar flask, both flasks being placed in a constant-temperature bath at 25°. When the temperature of the bath had been assumed, the mixed solutions were poured rapidly into the flask containing the iodide solution and then immediately returned to the first flask, both flasks then being replaced in the water-bath. The total volume of the reaction mixture was 100 cc. At the end of the chosen time interval, 25 cc. of a solution containing 110 g. of sodium acetate and 10 g. of sodium bicarbonate per liter was added to stop the reaction. The titration with sodium thiosulfate was then immediately made. A 5-cc. buret graduated to 0.02 cc. was used in making all titrations.

Calculation of the Velocity Constant

Since the concentrations of acid and iodide were greatly in excess over the dichromate, the velocity of reaction could be assumed to be proportional solely to the concentration of the latter. Under these conditions the work of DeLury, and of Kernot and Pietrofesa, and also the results presented in this paper, indicate pretty clearly that the reaction is first order with respect to dichromate (note the constant values of k in Tables III and IV). As a basis for the calculation, the "infinity" value for the reaction was taken as the average of the last two thiosulfate readings shown in Table I, Col. 3. The experimental results are exhibited in Table I and Fig. 1.

TABLE I

SHOWING THE SALT EFFECT ON THE FIRST-ORDER VELOCITY CONSTANT DUE TO VARYING CONCENTRATIONS OF SODIUM CHLORIDE FOR CONSTANT TIME INTERVALS OF TWENTY MINUTES

Initial H^+, **364** × 10^{-4} **M; I–, 142** × 10^{-4} **M;** $Cr_2O_7^{--}$, **2.02** × 10^{-4} *M*.

Expt.	C_{NaCl}, *M*	$Na_2S_2O_3$, 0.00986 *M*, cc.	2 + log k	$\sqrt{\mu}$ total
1	0.0	4.15	0.314	0.226
2	.01	3.93	.293	.247
3	.025	3.74	.259	.276
4	.10	3.22	.182	.388
5	.20	2.88	.126	.500
6	.40	2.68	.090	.671
7	.50	2 68	.090	.741
8	.60	2.82	.114	.806
9	.80	2.80	.112	.921
10	1.0	3.20	0.179	1.024
11	1.4	3.89	.279	1.204
12	1.8	4.86	.401	1.360
13	2.2	6.12	.537	1.500
14	2.6	7.61	.684	1.628
15	3.0	9.30	.849	1.746
16	4.0	12.29[a]		
17	5.0	12.08[a]		

[a] Reaction completed.

Discussion of Figure 1

In Fig. 1 the logarithm of the first-order velocity constant, k, is plotted against the square root of the ionic strength, $\sqrt{\mu}$. The rather surprising results obtained are difficult to interpret. In general, the curve in the figure is very similar to activity curves for strong acids when plotted as a function of $\sqrt{\mu}$. The minimum in the curve appears at an ionic strength of about 0.5, which is about the point at which the minimum occurs in activity curves for strong acids. Unfortunately, little is known concerning the variation of the activity of dichromate and hydriodic acid over this range of ionic strength. If data on this point were available it might be possible to interpret the minimum in the reaction velocity in more detail. However, in the light of Bronsted's theory it is possible to explain the results obtained in the more dilute solutions. For the detail of the Bronsted theory, the reader is referred to the original papers.[5] The following is a brief outline of some of the more essential features.

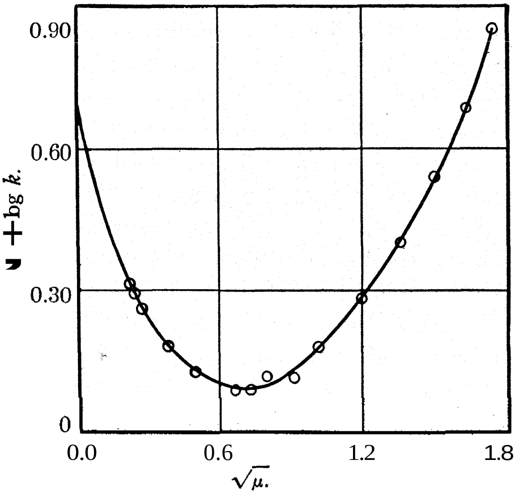

Fig. 1.—Curve showing the effect of neutral salt on the first-order constant, the initial concentrations of H^+, I^- and CrO_{27}^{--} being maintained constant throughout.

According to the classical theory, the expression for the velocity of reaction in the case of a trimolecular reaction may be written h = $k_1c_Ac_Bc_C$. The corresponding expression derived from the "activity theory" is h = $k_2a_Aa_Ba_C$. In these expressions c and a represent concentrations and activities, respectively. Bronsted drives the expression h = $kc_Ac_Bc_Cf_Af_Bf_C/f_x$ for a trimolecular reaction, where $f_Af_Bf_C$ and f_x denote the activity coefficients of A, B, C and x, respectively. x is a complex ion formed by the collision of A, B and C. Since in dilute solutions the activity coefficients of ions depend largely on the charges borne by the ions, and since the charge of x is the algebraic sum of the charges of A, B and C, the application of the Bronsted equation to the calculation of reaction velocities is made possible. Combining the Bronsted with the classical expression we obtain $k_1 = kf_Af_Bf_C/f_x$. For the calculation of the "kinetic activity

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[5] Bronsted, *Z. physik.* Chem., 102, 169 (1922); Bronsted, *ibid.*, 115, 337 (1925); Brönsted and Delbanco, *Z. anorg. Chem.*, 144,248 (1925).

factor," $f_Af_Bf_C/f_x$, the Debye expression,[6] $-\log f = Az^2\sqrt{\mu}$, may be employed. In this last equation z is the valence of a particular ion, μ is the ionic strength and the factor A has a value of about 0.5 and is so taken for the calculation. Bronsted's development finally leads to the relation: $\log k_1 = \log k + (z_Az_B + z_Az_C + z_Bz_C)\sqrt{\mu}$ for *a* trimolecular reaction. If now $\log k_1$ as ordinate is plotted against $\sqrt{\mu}$ as abscissa, a straight line should result with a slope equal to $(z_Az_B + z_Az_C + z_Bz_C)$ and with an intercept log k on the ordinate axis. Considerable evidence[7] has been presented in support of this theory, but so far as the authors are aware no previous attempt has been made to apply the Bronsted theory to trimolecular or more complex reactions.

Assuming for the sake of argument that our reaction is trimolecular, we may let A, B and C be $Cr_2O_7^{--}$, H^+ and I^-, respectively. Thus $z_A = -2$, $z_B = 1$, $z_C = -1$. Substituting these values in the above equation, it becomes, $\log k_1 = \log k + (-1)\sqrt{\mu}$. *A* plot of $\log k_1$ *versus* $\sqrt{\mu}$ would have a slope of (-1) under these conditions.

On the other hand, if the reaction be pentamolecular, as the work of DeLury and others and many of the experimental results obtained in the preliminary work of this research seem to indicate, it can be shown that this would lead to the equation

$$\log k_1 = \log k + (z_Az_B + z_Az_C + z_Az_D + z_Az_E + z_Bz_C + z_Bz_D + z_Bz_E + z_Cz_D + z_Cz_E + z_Dz_E)$$

Letting A represent $Cr_2O_7^{--}$, and B and C represent H^+, and D and E, I^-, the expression simplifies to $\log k_1 = \log k + (-2)\sqrt{\mu}$.

Later on in this paper evidence will be given showing that the reaction really consists of two simultaneous reactions, one involving $Cr_2O_7^{--}$, H^+ and I^- to the first power and the other involving $Cr_2O_7^{--}$ to the first power and H^+ and I^- to the second power. Furthermore, calculations

TABLE II

EFFECT OF VERY LOW SODIUM CHLORIDE CONCENTRATION ON THE FIRST-ORDER VELOCITY CONSTANT FOR CONSTANT TIME INTERVALS OF TWENTY MINUTES

Initial H^+, 364 X 10^{-4} *M;* I^-, 142 X 10^{-4} *M;* $Cr_2O_7^{--}$, 2.02 X 10^{-4} M.

Expt.	C_{NaCl}	$Na_2S_2O_3$, *cc.*	2 + log *k*	$\sqrt{\mu}$, total
1	0.00	3.74, 3.69, 3.84, 3.84 (av. 3.78)	0.271	0.226
2	.005	3.72, 3.70, 3.66, 3.72, 3.69 (av. 3.70)	.260	.237
3	.01	3.62, 3.60, 3.60, 3.66, 3.62 (av. 3.62)	.248	.247
4	.02	3.52, 3.50, 3.54, 3.49 (av. 3.51)	.232	.267
5	.03	3.34, 3.38, 3.30 (av. 3.34)	.210	.285
6	.04	3.27, 3.24, 3.31, 3.30 (av. 3.28)	.197	.302
7	.05	3.25, 3.22, 3.20, 3.20, 3.18 (av. 3.21)	.186	.318
8	.06	3.14, 3.15, 3.12, 3.16, 3.14 (av. 3.14)	.175	.333

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[6] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); Bronsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[7] Bronsted and Livingston, *ibid.*, 49, 435 (1927); Livingston and Bray, *ibid.*, 45, 2048 (1923); Brönsted and Delbanco, *Z* anorg. *Chem.*, 144,248 (1925).

from the data show that about 65% of the transformation is brought about by the pentamolecular reaction. Consequently, if a plot of log k_1 against $\sqrt{\mu}$ be made, the slope of the resulting line should be -1.65 at low ionic strength. The data of Table II were thus plotted in Fig. 2. It will be seen that the experimental curve is asymptotically tangent to the theoretical slope -1.65. The magnitude of the ionic strength in these experiments is, of course, too great to expect that the points would actually fall on a line with the theoretical slope. Actual coincidence of such experimental curves with the theoretical is only obtained at ionic strengths $\sqrt{\mu} = 0.15$ or less (see work of Bronsted cited above). Unfortunately, data are not available over a lower range of concentration owing to the marked slowing down of the reaction. Figs. 1 and 2 will be discussed further, later in the paper. Table II presents results of additional experiments in the more dilute sodium chloride solutions. Fresh solutions of the reactants were made up in practically the same concentration as before.

When Expts. 1 of Tables I and II are closely compared, it will be noted that different values for log k are obtained for solutions of the same ionic strength. This inconsistency was due to some undetermined source of error, perhaps caused by incorrect standardization of the sodium thiosulfate used in the second set of experiments. However, the error is a constant one and does not invalidate the conclusions drawn from the data. All of the runs in Table II were performed within a few days and it is improbable that any change occurred in the strength of the thiosulfate during that period.

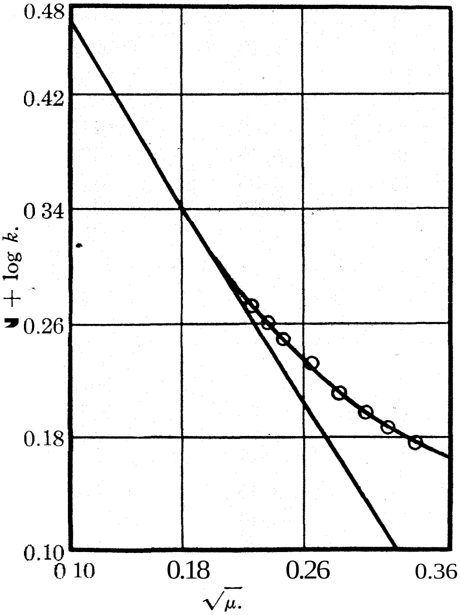

Fig. 2.—Showing the variation in the first-order constant with the sodium chloride concentration. The curve approaches a theoretical tangent of about -1.65.

Experiments at High Neutral Salt Concentration

In carrying out this series of experiments, the data from which are given in Table III, 1.5 M sodium chloride solution was used in each of the seven runs, the first four involving change of iodide concentration only and the last three change of acid concentration. The concentration of the dichromate was 2.02×10^{-4} *M* in all the runs. Table IV gives similar data for three runs in which no salt was added.

TABLE III

SHOWING VELOCITY OF REACTION WITH THE DICHROMATE CONCENTRATION LOW AND VARYING THE IODIDE AND ACID CONCENTRATIONS IN TURN. 1.5 M SODIUM CHLORIDE

Run 8. Init. C_{KI}, 142×10^{-4} *M*. Init. C_{HClO_4}, 364.8×10^{-4} M. Av. $k/(H^+)^2(I^-)^2$, 8.20×10^4

Time, min.	0 00986 *M* $Na_2S_2O_3$, cc.	k
5	1.18	0.0202
10	2.22	.0197
15	3.19	.0203
20	3.96	.0177
30	5.40	.0190
45	6.98	.0174
75	9.29	.0190
120	10.98	.0184

Run 9. Init. C_{KI}, 71.0×10^{-4} *M*. Init. C_{HClO_4}, 364.8×10^{-4} M. Av. $k/(H^+)^2(I^-)^2$, 11.66×10^4

Time, min.	0 00986 *M* $Na_2S_2O_3$, cc.	k
5	0.44	0.0073
10	0.88	.0076
15	1.35	.0084
20	1.70	.0065
30	2.44	.0072
45	3.40	.0068
75	5.10	.0071
120	6.50	.0052

Run 11. Init. C_{KI}, 106.5×10^{-4} *M*. Init. C_{HClO_4}, 364.8×10^{-4} M. Av. $k/(H^+)^2(I^-)^2$, 9.76×10^4

Time, min.	0 00986 *M* $Na_2S_2O_3$, cc.	k
5	0.86	0.0145
10	1.58	.0130
15	2.30	.0139
20	3.02	.0150
30	4.10	.0124
45	5.42	.0117
75	7.38	.0112
120	9.38	.0116

Run 10. Init. C_{KI}, 284×10^{-4} *M*. Init. C_{HClO_4}, 364.8×10^{-4} M. Av. $k/(H^+)^2(I^-)^2$, 6.85×10^4

Time, min.	0 00986 M $Na_2S_2O_3$, cc.	k
5	3.36	0.0640
10	5.81	.0642
15	7.62	.0655
20	8.91	.0647

Run 12. Init. C_{KI}, 142×10^{-4} *M*. Init. C_{HClO_4}, 181.2×10^{-4} M. Av. $k/(H^+)^2(I^-)^2$, 10.30×10^4

Time, min.	0 00986 M $Na_2S_2O_3$, cc.	k
10	0.72	0.0068
15	1.08	.0063
20	1.45	.0067
33	2.20	.0055
45	2.93	.0063
75	4.46	.0060

Run 13. Init. C_{KI}, 142×10^{-4} *M*. Init. C_{HClO_4}, 273×10^{-4} M. Av. $k/(H^+)^2(I^-)^2$, 9.20×10^4

Time, min.	0 00986 M $Na_2S_2O_3$, cc.	k
5	0.80	0.0135
10	1.48	.0122
15	2.14	.0126
30	2.98	.0102
45	3.88	.0114
75	5.20	.0115
120	7.27	.0128

Run 14. Init. C_{KI}, 142×10^{-4} M. Init. C_{HClO_4}, 454.2×10^{-4} M. Av. $k/(H^+)^2(I^-)^2$, 8.09×10^4

Time, min.	0 00986 M $Na_2S_2O_3$, cc.	k
5	1.81	0.0319
10	3.27	.0300
20	5.68	.0269
30	7.39	.0299
57	9.98	.0279

As before, the values of k were calculated on the assumption that the velocity of the reaction was proportional solely to the concentration of the dichromate, owing to the fact that the concentration of the other two reactants was high in comparison to that of the dichromate. The assumption of fixed H^+ and I^- is not entirely justified, particularly in Runs 9 and

TABLE IV

SHOWING VELOCITY OF REACTION WITH THE DICHROMATE CONCENTRATION LOW AND VARYING THE ACID CONCENTRATION ONLY. NO NEUTRAL SALT ADDGD

Run 1R. Init. I^-, 142 X 10^{-4} *M*. Init. H^+, 730 X 10^{-4} *M*. $Na_2S_2O_3$, 0.01032 N. Av. $k/(H^+)^2(I^-)^2$, 11.78 X 10^4

Time in minutes	5	10	15	20
$Na_2S_2O_3$ used, cc.	4.70	7.42	9.32	10.34
k	0.1023	0.0976	0.1159	0.1095

Run 2R. Init I^-, 142 × 10^{-4} *M* Init. H^+, 547.6 × 10^{-4} *M*. $Na_2S_2O_3$, 0.01029 N. Av. $k/(H^+)^2(I^-)^2$, 9.55 X 10^4

Time in minutes	6	10	15	20	30	45
$Na_2S_2O_3$ used, cc.	3.00	4.60	6.06	7.26	9.02	10.52
k	0.0490	0.0503	0.0455	0.0472	0.0495	0.0526

Run 3R. Init. I^-, 142 X 10^{-4} *M*. Init. H^+, 365.1 X 10^{-4} M. $Na_2S_2O_3$, 0.01007 N. Av. $k/(H^+)^2(I^-)^2$, 8.24 × 10^4

Time in minutes	5	10	15	20	30	45
$Na_2S_2O_3$ used, cc.	1.14	2.18	3.02	3.86	5.38	7.20
k	0.0199	0.0201	0.0178	0.0196	0.0206	0.0213

12, as may be seen by comparing the concentrations in Table III. However, in evaluating the expression $k/(H+)^2(I^-)^2$, used in Figs. 3, 4, 5 and 6, a correction was made to take into account the change in iodide and hydrogen-ion concentration during the course of a run. This was made by

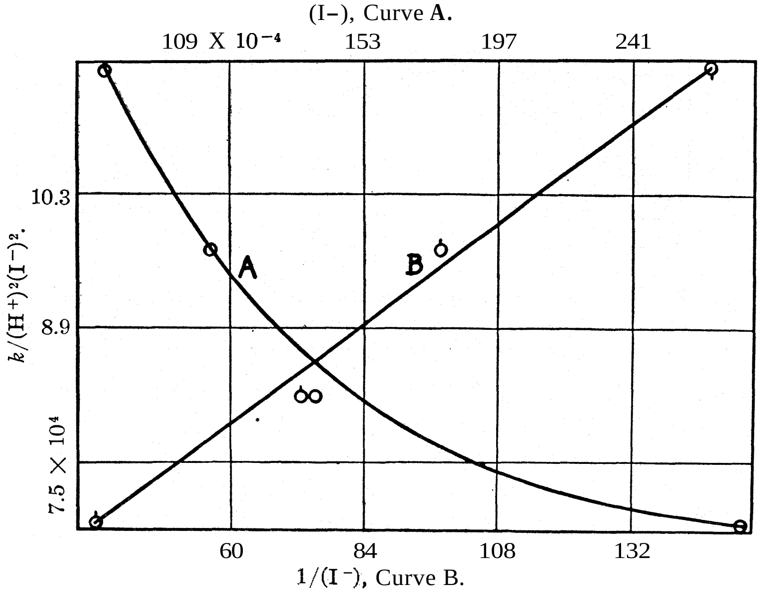

Fig. 3.—Curve A shows that the reaction is not second order with respect to (I^-). Curve B shows that the reaction consists of two simultaneous reactions, one involving (I–) and the other $(I^-)^2$.

calculating the concentration of the iodide and acid left at the end of each time interval and dividing the product of the squares of these values into the corresponding value for *k* previously determined. The following example shows the method of calculation. In Run 10 the iodide used up in the first five minutes was equivalent to 3.36 cc. of 0.00986 N sodium thiosulfate. Consequently, $3.36 \times 0.00986 \times 10^{-3} = 3.31 \times 10^{-5}$ (the number of moles used up in 100 cc. of the reaction mixture), or 3.31×10^{-4} per 1000 cc. of the reaction mixture. The concentration of the iodide at the end of the first five minutes will then be equal to 284×10^{-4} minus 3.31×10^{-4} or 280.69×10^{-4} moles per liter. Multiplying 3.31×10^{-4} by 7/3 and subtracting from 364.8×10^{-4} will give the concentration of the acid at the end of the first five minutes, 357.07×10^{-4} moles per liter. The corresponding value of the velocity constant is seen to be 0.0640. Consequently $k/(H^+)^2(I^-)^2 = 0.0640/(280.69)^2(357.07)^2(10^{-8})^2 = 6.39 \times 10^4$.

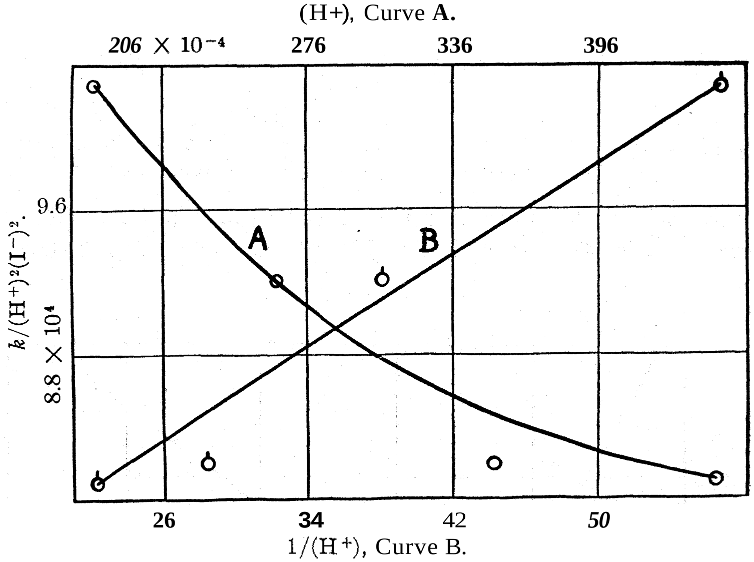

Fig. 4.—Curve A shows that the reaction is not second order with respect to (H^+). Curve B shows that the reaction consists of two simultaneous reactions, one involving (H^+) and the other $(H^+)^2$.

While the usual method is to use the initial values of the concentration of those reactants which are in excess, we believe that this method of calculation is a more accurate treatment of the experimental results. In Table V is given the average value of $k/(H^+)^2(I^-)^2$ for each run, computed in this way, as well as the other data used in Figs. 3, 4, 5 and 6.

In Fig. **3** are shown plots of these values against the iodide concentration (Curve A) and against the reciprocal of the iodide concentration (Curve B) for Runs 8, 9, 10 and 11. Curve A, Fig. 3, shows that the reaction is not

TABLE V

VALUES USED IN FIGURES 3, 4, 5 AND 6

Run	Av. H^+ $\times 10^4$	Av. $1/H^+$	Av. I^- $\times 10^4$	Av. $1/I^-$	Av.$(1/H^+)$-$(1/I^-) \times 10^{-3}$	Av. $k/(H^+)^2$-$(I^-)^2 \times 10^{-4}$
1R	711.1	14.06	133.5	74.90	..	11.78
2R	531.4	18.82	135.1	74.02	..	9.55
3R	356.2	28.07	138.2	72.36	..	8.24
8	352.4	28.38	136.6	73.22	2.08	8.20
9	358.5	27.89	68.3	146.4	4.09	11.66
10	350.0	28.57	277.7	36.05	1.03	6.85
11	355.0	28.16	102.3	97.75	2.76	9.76
12	176.3	56.73	139.9	71.47	4.05	10.30
13	262.4	38.12	137.7	72.62	2.77	9.22
14	441.3	22.66	136.5	73.26	1.66	8.09

second order with respect to iodide concentration, because if this were so $k/(H^+)^2(I^-)^2$ would be constant from run to run and a straight horizontal line would be obtained in the plot. If two simultaneous reactions were going on here, one of which was first order and the other second order

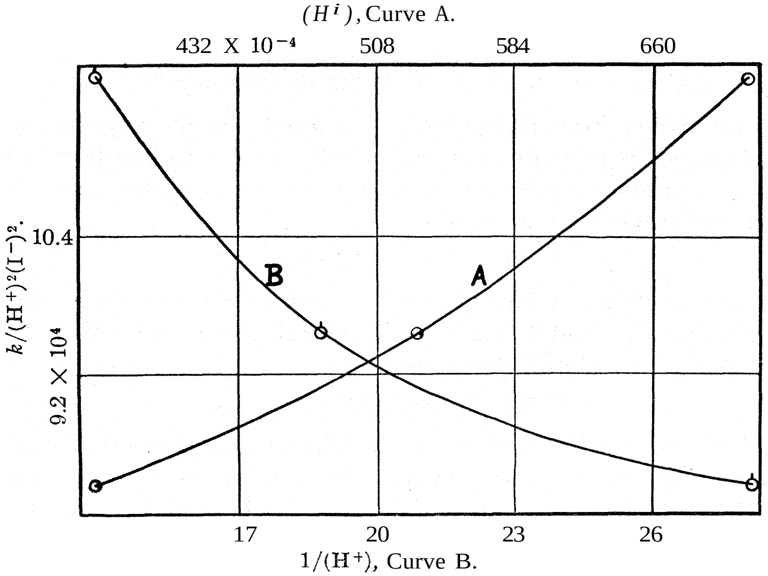

Fig. 5.—Showing that no simple interpretation of the data is possible in the absence of neutral salt. Straight line relations are not obtained.

with respect to I–, the general expression for the velocity constant would be $k = k_1I^- + k_1k_2(I^-)^2$. Dividing through by $(H^+)^2 \times (I^-)^2$, this expression becomes $k/(H^+)^2(I^-)^2 = k_1/(H^+)^2(I^-) + k_1k_2/(H^+)^2$. Consequently, if $k/(H+)^2(I^-)^2$ be plotted against $1/(I^-)$, a straight line should be obtained, since in the four series of experiments the concentration of acid was not varied. In Curve B, Fig. 3, the points fall approximately on a straight line.

The data for Runs 8, 12, 13 and 14 were treated similarly with results as shown in Fig. 4. Curve A shows that the reaction is not second order with respect to (H^+). Curve B indicates that the reaction is really composed of two simultaneous reactions, one of which is first order and the other second order with respect to (H^+).

Figure 5 shows the results of similar plots in the case of Runs 1R, 2R and 3R. Again Curve **A** is the plot of $k/(H^+)^2(I^-)^2$ against H^+, while curve B is the plot against $1/H^+$. Here it is seen that neither curve is capable of any simple interpretation. In this series of experiments no salt was present to-fix the activity coefficients. Not only is Curve B not a straight line, but even the direction of B is reversed, the slope being negative instead of positive. The slope is also reversed in A. A comparison of Figs. 4 and 5 clearly indicates the beneficial effect of adding a neutral salt in making velocity studies of this type. It is important to note that the data in the absence of salt are incapable of any simple interpretation, as may be seen from Fig. 5, but when salt is added the difficulties of interpretation disappear as seen from the straight-line relation in Fig. 4.

Rate Constants for the Two Simultaneous Reactions

The discussion from this point bears entirely on the experimental results obtained in presence of 1.5 M NaCl. If the assumption is made that two simultaneous reactions occur, the observed velocity constant may be split into two factors, as follows

$$k = k_a(H^+)(I^-) + k_ak_b(H^+)^2(I^-)^2$$

where one reaction involves H^+ and I^- each to the first power and the other involves H^+ and I^- each to the second power. Dividing through by $(H^+)^2(I^-)^2$, we obtain the relation

$$k/(H^+)^2(I^-)^2 = k_a/(H^+)(I^-) + k_ak_b$$

where k_a is the velocity constant for the trimolecular reaction and k_ak_b the corresponding velocity constant for the pentamolecular reaction. In Fig. 6 the "5th order constant" $k/(H^+)^2(I^-)^2$ has been plotted as a function of $1/(H^+)(I^-)$. It follows from the equation just given that the slope of the best straight line through these points should be k_a. This has a value of 14.62. The pentamolecular constant has been evaluated from the data and found to be $k_ak_b = 53{,}000$. Taking these values as correct, one may calculate what the "observed velocity constant" should be to give exact agreement with this line. The data are recorded in Table VI. The calculated values of k were obtained from the straight line of Fig. 6 by picking off the values of $k/(H^+)^2(I^-)^2$ corresponding to the different values of $1/(H^+)(I^-)$ and solving for k.

TABLE VI

VELOCITY CONSTANTS IN RUNS INVOLVING 1.5 M NaCl

Run	8	9	10	11	12	13	14	
Av. k, obs.	0.0189	0.0070	0.0646	0.0127	0.0063	0.0122	0.0293	
Av. k, calcd.	0.0195	0.0068	(0.0646)	0.0124	0.0068	0.0123	0.0283	
Deviation, %	3.0	3.0	0.0	2.0	7.0	1.0	3.5	**Av.,** 3.0

The average percentage deviation of 3% is within the limit of error for the actually observed constants, k.

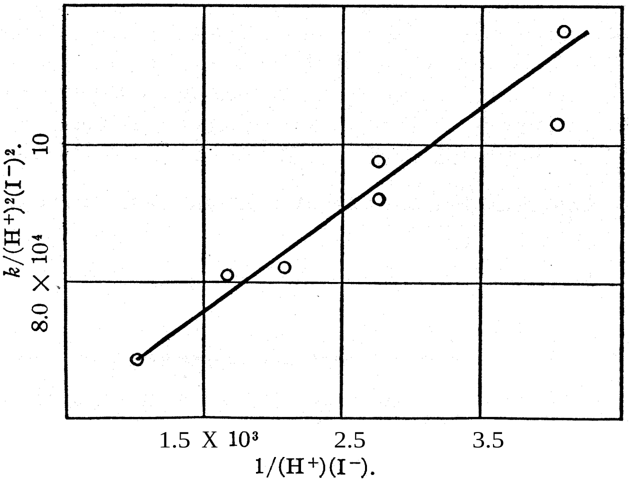

Fig. 6.—A combination of the two B curves in Figs. 3 and 4, showing that the reaction consists of two simultaneous reactions, one involving (H^+) and (I^-), the other $(H^+)^2$ and $(I^-)^2$.

Discussion of Figures 1 and 2

In the experiments recorded in Table II and Fig. 2, on the effect of varying sodium chloride concentration on the reaction velocity, the H^+ and I^- ion concentrations were 0.03643 and 0.0142 M, respectively. Substituting these values in the equation $k = 14.6(H^+)(I^-) + 53{,}000(H^+)^2(I^-)^2$, one obtains the following result, $k = 0.0076 + 0.0142$. Thus, μ being 1.55, the fraction $0.0142/(0.0142 + 0.0076) = 0.651$ (or about 65%) of the iodide is oxidized by the pentamolecular reaction.

As will be seen from an inspection of Fig. 1, the rate is practically the same in solutions of ionic strength ranging from $\sqrt{\mu} = 0.1$ to $\sqrt{\mu} = 0.2$ as it is in a 1.5 M sodium chloride where $\mu = 1.55$ or $\sqrt{\mu} = 1.25$. If hydriodic acid is like hydrochloric acid, the activity coefficient of hydriodic acid (i. e., $f_H f_I$) is also practically the same in these two solutions, namely, about 0.9. It is a consequence of the Bronsted theory that the ratio of the pentamolecular to the trimolecular rate will be proportional to $f_H f_I$.[8]

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[8] $h_5/h_3 = [(H^+)(I^-)k_5/k_3]f_{H^+}f_{I^-}$.

Consequently, about 65% of the oxidation should take place by the pentamolecular reaction in *the dilute solution.* The theoretical Brönsted slope should therefore be not -1 nor -2 but about -1.65, and is so drawn in Fig. 2. The lowest ionic strength investigated, $\sqrt{\mu} = 0.226$, is still too high for the simple Debye–Hückel equation to apply, but the trend of the experimental curve is such as to indicate -1.65 as being a reasonable value for the limiting slope in the most dilute solutions. It is therefore felt that Bronsted's treatment gives the correct interpretation of the experimental data in the less concentrated sodium chloride solutions. We do not wish to claim that -1.65 is the exact limiting slope, since $f_H f_I$ increases from about 0.9 to 1 as the ionic strength changes from $\sqrt{\mu} = 0.15$ to $\sqrt{\mu} = 0$, but merely to emphasize the point that on account of the two simultaneous reactions the limiting slope cannot be an integral number. However, the limiting slope cannot be far from -1.65.

Discussion of the Probable Chemical Changes

DeLury[3] has stated that his measurements indicate the possibility of two simultaneous reactions which affect the measured rate. Bray[9] has suggested that these may be

$$2I^- + 2H^+ + Cr_2O_7^{--} = 2IO^- + H_2Cr_2O_5 \qquad (1)$$

$$I^- + 2H^+ + Cr_2O_7^{--} = IO^- + 2HCrO_3 \qquad (2)$$

It is evident from the experimental results presented in this paper that Reaction 2 involving $2H^+$ ions per I^- ion cannot be a slow reaction and affect the rate. If this were so the plot of $k/(H^+)^2(I^-)^2$ against H^+ in Fig. 4 would be a horizontal straight line or, in other words, the "5th order constant," $k/(H^+)^2(I^-)^2$ would be independent of the H^+ ion concentration. Fig. 4 shows a definite linear relation of $k/(H^+)^2(I^-)^2$ to $1/H^+$.

The fact that a satisfactory representation of the experimental results in high neutral salt concentration is given by the equation

$$k = 14.6\,(H^+)(I^-) + 53{,}000\,(H^+)^2(I^-)^2$$

indicates that the two slow steps in the reaction are probably

$$(I)\quad H^+ + I^- + Cr_2O_7^{--} \longrightarrow \text{..} \quad \text{and}$$

$$(II)\quad 2H^+ + 2I^- + Cr_2O_7^{--} \longrightarrow \text{......}$$

Although the experimental evidence points clearly to the occurrence of a tri- and a pentamolecular reaction, it is not necessary to assume the simultaneous collision of more than two molecules. Starting with the Bronsted rate equations for only rapid reversible *bimolecular* reactions, one may readily combine them to obtain the correct kinetic equations for reactions of the third and fifth order, which satisfy the experimental data. The following equations were thus obtained

$$k_3 = k_3(H^+)(I^-)(Cr_2O_7^{--}) \times f_{H^+}f_{I^-} \times f_{Cr_2O_7^{--}}/f_{X_1^{--}}$$

$$k_5 = k_5(H^+)^2(I^-)^2(Cr_2O_7^{--}) \times f^2_{H^+} \times f^2_{I^-} \times f_{Cr_2O_7^{--}}/f_{X_2^{--}}$$

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[9] *Bray, Z. physik. Chem., 54, 491 (1906).*

Summary

Measurements have been made on the velocity of the stoichiometrical reaction $Cr_2O_7^{--} + 6I^- + 14H^+ = 2Cr^{+++} + 7H_2O + 3I_2$ at various concentrations of the reacting ions and in presence and absence of a neutral salt, sodium chloride. All experiments were carried out at 25°.

In dilute solutions the results offer confirmation of the Bronsted activity rate theory of reaction velocity.

In more concentrated solutions in the absence of a neutral salt, the kinetic behavior is incapable of any simple interpretation.

In the presence of 1.5 M sodium chloride as neutral salt, the kinetic anomalies disappear. The experimental results clearly indicate that two simultaneous reactions are taking place which may be represented as follows

$$H^+ + I^- + Cr_2O_7^{--} \longrightarrow HI\cdot Cr_2O_7^{--} \qquad (1)$$

$$2H^+ + 2I^- + Cr_2O_7^{--} \longrightarrow (HI)_2\cdot Cr_2O_7^{--} \qquad (2)$$

The observed velocity constant k is given to within an accuracy of 3% by the expression $k = 14.6\,(H^+)(I^-) + 53{,}000\,(H^+)^2(I^-)^2$.

MINNEAPOLIS, MINNESOTA

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

THE RATE OF RECOMBINATION OF ATOMIC HYDROGEN

BY HUGH M. SMALLWOOD

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It has been pointed out by a number of investigators[1] that certain exothermic reactions of the type A + B ⟶ AB cannot result from simple binary collisions of molecules A and B since, in such a collision, there is no means by which the energy corresponding to the heat of the reaction may be removed from the colliding molecules. In order to react the molecules must collide in the immediate neighborhood of some other object such as another molecule or the wall of the containing vessel. In other words, the reaction can only take place as the result of triplet impacts or three-body collisions.

A few limitations must be made to the foregoing statement. Thus, if there is a possibility of radiation occurring during the collision of molecules A and B, combination may result from a single collision since the energy of combination may be radiated from the system as light. Further, if molecules A and B are relatively complex, the energy of combination may be taken up by their internal degrees of freedom.

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[1] Boltzmann, "Gastheorie. II," Leipzig, 1912; Herzfeld, *Z. Physik*, 8, 132 (1922); Born and Franck, *Ann. Physik*, **76**, 225 (1925); *Z. Physik*, 31, 411 (1925); J. H. Jeans, "The Dynamical Theory of Gases," 4th ed., Cambridge University Press, p. 195.

There are therefore only a few reactions which may be expected to proceed according to the predicted three-body mechanism. One of these, however, is the recombination of atomic hydrogen, represented stoichiometrically by the reaction $H + H \longrightarrow H_2$. The present paper describes a measurement of the rate of this reaction at various pressures. The results obtained are in agreement with the predicted mechanism.

The method used was to allow dissociated hydrogen drawn from an electric discharge to pass along a straight tube.[2] The degree of dissociation of the hydrogen at varying distances along this tube was determined by measuring the heat effect produced upon a piece of platinum foil placed in the flowing gas at the desired distance from the discharge. Wood[2] has shown that metals cause the complete recombination of the atomic hydrogen. Since the heat of this recombination is known and since the rate of flow can be measured, the degree of dissociation is readily calculated.

Experimental

Source of Hydrogen.—Throughout these experiments the hydrogen was taken from a water-cooled electrolytic generator using as electrolyte a 30% solution of potassium hydroxide containing a little barium hydroxide. The hydrogen so obtained contains about 3% of water vapor. Since the presence of this water vapor has been shown to be necessary for the production of the atomic hydrogen, no attempt was made to remove it.

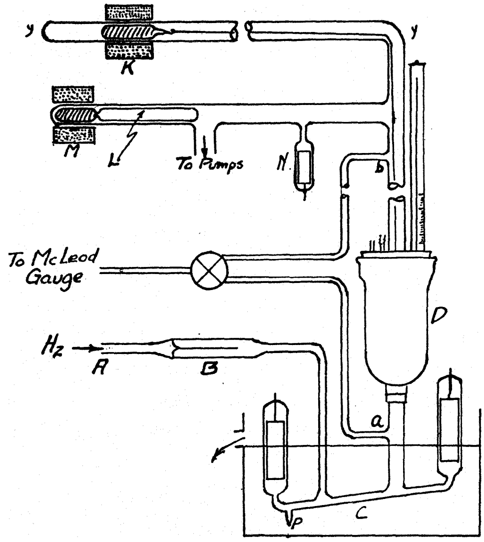

Fig. 1.

Apparatus.—Figure 1 shows the essential parts of the apparatus finally adopted. Hydrogen from the generator (not shown) was admitted at A and expanded through the capillary B to a pressure of a few tenths of a millimeter. It was then led to the discharge tube C, which was immersed in a water-bath. While in the discharge tube the hydrogen was almost completely dissociated, so that recombination took place along the vertical tube, ab. The pressure at each end of this tube could be measured on a McLeod gage by means of the connections shown in the sketch. D is a calorimeter (shown in detail in Fig. 2) which could be slid up or down the tube ab. The calorimeter was made in the shape of a small Dewar flask with a hole in the bottom, the joint between the calorimeter and the central tube ab being made water tight by means of a short piece of gum tubing, E. The calorimeter was flared slightly at the top to permit the insertion of a rubber stopper

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[2] R. W. Wood, Proc. Roy. *Soc.* London, 97A, 455 (1920); **102A,** 1 (1925); ***Phil. Mag.,*** 42, 729 (1921); 44, **538** (1922); Bonhoeffer, *Z. physik.* ***Chem.,*** 113, 199 (1924).

carrying a stirrer, F, a Beckmann thermometer, G, and a platinum heating unit, H, used to determine the heat capacity of the calorimeter. J was the catalytic surface causing the recombination of the atoms of hydrogen. It consisted of a cylinder of platinum foil fitting snugly inside the central tube and suspended from a fine nickel wire. The other end of this wire was fastened to a glass tube containing soft iron which could be moved along the tube yy by means of the electromagnet K (Fig. 1). In this way the platinum could be moved along the central tube with the calorimeter. The pressure in the apparatus was regulated by sliding the core I, into or out of the gas stream by means of the electromagnet M. N is an auxiliary electrode whose use will be described below.

The tube ab was approximately one meter long and 0.8 cm. in internal diameter. The discharge tube was made of thin-walled 0.6-cm. tubing to facilitate cooling, the distance between the inlet and outlet taps being about 10 cm. The distance between the discharge and tap a was 8 cm. The electrodes were the usual cylinders of aluminum foil fastened to tungsten wires which were sealed through the pyrex. Rapid streams of water played over the exposed ends of the electrodes, thus preventing the conduction of heat from the discharge to the calorimeter. The volume of the calorimeter was slightly greater than 100 cc. The calorimeter stirrer was rotated by a small electric fan motor.

Procedure.—The primary consideration for experiments with atomic hydrogen is that the regions where it is to be produced and studied must be absolutely free from substances which may catalyze the recombination. Apparently all metals are active catalysts, together with porous or adsorbent surfaces. With this in mind the apparatus was designed to permit washing in *situ*. Each apparatus was made from new pyrex glass. After complete assembly aqua regia was forced through the arm P up to the top of the tube ab and then allowed to drain back. Of course, during the washing the platinum catalyst J was lifted out of range of the acid. The apparatus was then rinsed repeatedly with distilled water, after which the arm P was sealed off and the pump started. Before making any runs a discharge was passed from the auxiliary electrode N to the discharge tube. Bonhoeffer[2] has previously shown that this is useful in preparing a catalytically inert tube.

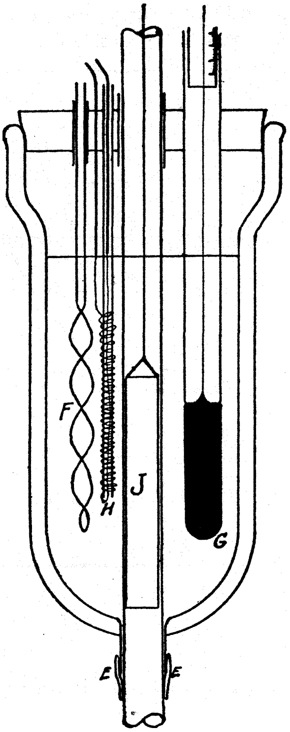

Fig. 2.

The foregoing procedure has been found in practically every instance to give apparatus in which reproducible results can be obtained. Presumably the aqua regia removes any metallic dust from the tube wall, the water fills up the pores in the wall and the discharge melts into the glass any active spots not removed by the acid. The discharge tubes show a pronounced fatigue effect after twenty to thirty hours of running. This fatigue is gradual and coincident with the appearance of appreciable quantities of sputtered material from the electrode. No successful method has so far been found for rejuvenating a spent tube.

The actual measurements were carried out as follows. The calorimeter and catalyst were set at the desired distance from the discharge and the pressure was allowed to reach the desired value; 100 cc. of distilled water, one or two degrees below room temperature, was pipetted into the calorimeter and the stirrer started. After the warming of the calorimeter had reached a steady rate the Beckmann thermometer was read at one-minute intervals (timed by an electric clock) for a period of five minutes, in order to obtain the rate of warming at the start of the run. At the end of this period the discharge was turned on and the temperature readings were continued until the temperature rise was great enough to ensure the desired accuracy. This required ten minutes or less. The temperature measurements were continued for five minutes after the discharge was turned off to determine the final cooling curve. Fig. 3 shows several typical temperature–time curves. The pressure in the apparatus was measured at points a and b twice each during each run. The room temperature was maintained constant within 0.5° throughout each run.

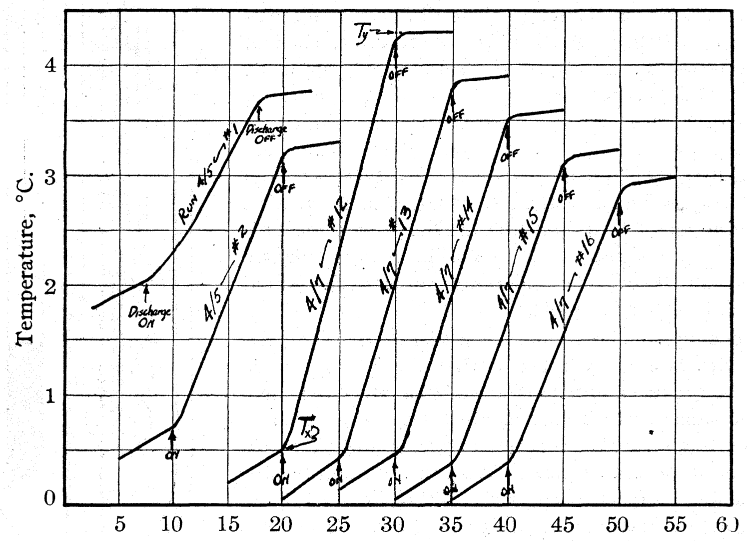

Fig. 3.

The heat capacity of the calorimeter was determined by noting the temperature rise caused by passing a current through the heating unit, H, the power input being measured by means of a milliammeter and millivoltmeter. The rate of flow of hydrogen was measured by disconnecting the hydrogen generator and allowing the hydrogen to be drawn instead from a gas buret.

Results

A series of preliminary experiments showed the qualitative conditions that must be fulfilled for the best production of atomic hydrogen. Aside from the necessity of the absence of catalysts, all the other variables affect the degree of dissociation of the hydrogen at a point some distance from the discharge. Thus the degree of dissociation is increased by high current density in the discharge and by water cooling the discharge. These two factors are, however, of secondary importance compared to the pressure and the quantity of hydrogen flowing. If the pumping capacity is approximately constant, these last two quantities are roughly proportional, the pressure increasing if the quantity of hydrogen admitted to the apparatus is increased. Since the degree of dissociation at a point removed from the discharge decreases rapidly as the pressure increases, there will be some set of conditions for each apparatus at which the greatest *amount* of atomic hydrogen is obtained at a point outside the discharge. The pressure and the rate of flow at which the greatest amount of atomic hydrogen is obtained are determined by the efficiency of the pumps and the dimensions of the apparatus.

The best series of measurements of the rate of recombination are summarized in Table I and plotted in Fig. 4. The degree of dissociation is expressed by α, the fraction of the total amount of hydrogen which is present in the atomic form x cm. from the point of measurement of the initial pressure (P_0).

TABLE I

RESULTS OF MEASUREMENTS

Rate of flow of $H_2 = n_0 = 1.03 \times 10^{-5}$ moles/second. Primary current to transformer = 25 amps. Internal diameter of tube ab = 0.848 cm. Length ab = 108.3 cm. Heat capacity of calorimeter = C = 121.5 Cal./deg.

Date	No.	Dist from a to calorim. x (cm)	Press. (mm. Hg) meas. at a, P_0	b, P_1	Temp. rise in calorim. °C. T_{obs}.	T_{corr}.	Dissociation, 100 α, %
4/5	1"	86.2	0.524	0.150	2.53	1.62	31.6
	2*	86.2	.514	.142	2.51	2.14	41.8
	3	86 2	.584	290	2.23	1.79	35.0
	4	86 2	.632	.356	2.04	1.48	29.0
	5	86.2	.714	.494	1.75	1.03	20.2
	6	86.2	.798	.584	1.23	0.77	15.1
	7	86.2	.508	.138	3.10	2.43	47.5
	8	65.9	.508	.140	3.43	2.73	53.4
	9	65.9	.642	.360	2.66	1.94	38 0
	10	65.9	.716	.484	2.36	1.44	28.2
	11	65.9	.788	.583	2.00	1.11	21.7
	12	65 9	.874	.684	1.44	0.87	17 0
	13	65.9	.508	.142	3.48	2.69	52.7
4/7	1*	65.9	.498	.134	3 27	2.57	50.3
	2	47.6	.488	.132	3.69	2.94	57.5
	3	47.6	.622	.360	2.98	2.25	44.0
	4	47.6	.696	.468	2.59	1.83	35.8
	5	47.6	.766	.568	2.33	1.45	28.4
	6	47.6	.850	.666	2.11	1.16	22.7
	7	31.6	.476	.136	3.25	3.23	63.2
	8	31.6	.616	.366	3.35	2.53	49.5
	9	31.6	.688	.474	2.73	2.25	44.0
	10	31.6	.762	.568	2.49	1.93	37 8
	11	31.6	.874	.666	2.08	1.53	29.9
	12	18.8	.488	.132	3.77	3.43	67.1
	13	18.8	.622	.364	3.43	3.01	58.9
	14	18.8	.694	.474	3.10	2.74	53.6
	15	18.8	.780	.570	2.79	2.39	46.8
	16	18.8	.834	.672	2.13	2.08	40.7

TABLE I (*Concluded*)

Date	No.	Dist. from a to calorim. x (cm.)	Press. (mm. Hg) meas. at		Temp. rise in calorim. °C.		Dissociation, 100 α, %
			a, P_a	b, P_1	$T_{obs.}$	$T_{corr.}$	
4/10	1	18.8	.502	.148	3.62	3.52	68.8
	2	8.3	.504	.148	3.93	3.89	76.1
	3	8.3	.642	.374	3.56	3.62	70.8
	4*	8.3	.708	.500	2.58	2.50	49.1
	5	8.3	.784	.578	3.06	2.96	57.9
	6	8.3	.864	.678	2.99	2.86	56.0
	7	8.3	.710	.490	3.35	3.38	66.2
	8	1.4	.496	.142	3.71	4.10	80.2
	9	1.4	.638	.394	3.39	3.91	76.5
	10	1.4	.710	.490	3.51	3.76	73.6

The pressures recorded are each the average of two readings taken during the particular run. During each of the runs the discharge was on for ten minutes except Run 4/7 No. 7, the time of which was eight minutes. The temperature–time readings were plotted on a large scale as soon as obtained.

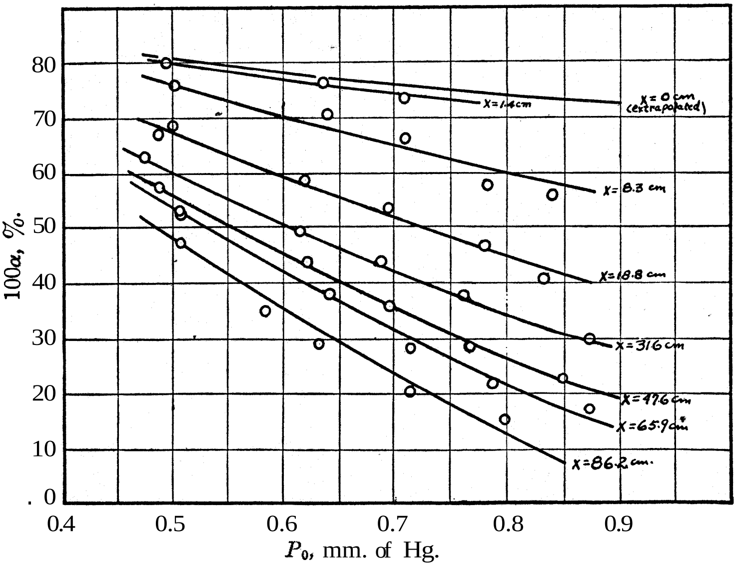

Fig. 4.

The observed temperature rise was obtained by subtracting the temperature at the start of the period when the discharge was on from the temperature obtained by extrapolation of the final cooling curve back to the time at which the discharge was turned off ($T_{obs.} = T_y - T_x$, Fig. 3). The correction for radiation and conduction of heat to or from the surroundings and for the heat of stirring was obtained by averaging the rate of cooling at the start and at the end, multiplying this average rate by the time during which the discharge was on and adding or subtracting, as the case might be, to the observed temperature rise. The figures so obtained are tabulated under the heading "$T_{corr.}$"

The fraction dissociated was calculated from the relation

$$\alpha = \frac{CT_{corr.}}{60\, n_0 t \Delta H} \tag{1}$$

where ΔH is the heat of formation of one mole of molecular hydrogen from the atoms. This quantity was taken to be 100,400 Cal., which is an average of the values reported by Dieke and Hopfield,[3] and Witmer[4] from studies of the molecular spectrum of hydrogen. The "t" of Equation 1 stands for the time in minutes during which the discharge was on. The other symbols have the meanings assigned in Table I.

It will be noticed that the starred (") runs of Table I are omitted from the plot of Fig. 4, since it was apparent from the varying slopes of the respective temperature–time curves that conditions changed during these runs. This discrepancy is of common occurrence and is undoubtedly due to a temporary catalytic effect. For example, if the apparatus is filled with air and left overnight, it requires from fifteen to twenty minutes' running before the degree of dissociation of the hydrogen outside the discharge builds up to a reproducible value, possibly due to a slow clean-up of oxygen adsorbed on the glass. This effect accounts for the first three inconsistent runs of Table I. It is readily recognized on the temperature–time curve, as may be seen by comparing the first two curves of Fig. 3. It is not evident in the first experiment of the third day since the discharge was run for thirty minutes before the runs were started. The other inconsistent run may have been caused by a catalytic particle working into the discharge and then being rendered inactive. It must be emphasized that, once active catalysts have been removed, the results do not depend on the apparatus. Duplicate runs which checked well within the experimental error have been made in different apparatus and at intervals of several weeks.

As will be pointed out below, an interpretation of the results requires a knowledge of the manner in which the pressure varied along the tube ab. An attempt was made to measure this, at the conclusion of the experiments, by sealing a number of taps into the tube and connecting these taps through stopcocks to the McLeod gage. The results so obtained are shown in Fig. 5, the dotted portions of the curves corresponding to the pressure drop caused by the presence of the platinum foil. Unfortunately some catalytic substance must have been present during these runs because the curves corresponding to the dissociated gas have the same slope as those for the molecular hydrogen. This would mean that the mixture of atomic and molecular hydrogen has the same viscosity as pure molecular

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[3] Dieke and Hopfield, *Z. Physik*, 40,299 (1926).

[4] Witmer, *Phys. Rev.*, 28, 1223 (1926).

hydrogen. That this is not the case has been shown by Harteck.[5] It is much more probable that very little atomic hydrogen reached the Tube ab due to the presence of an active catalyst. There was no way of checking this point since the calorimeter was necessarily removed during the remodeling of the apparatus.

It was hoped at first that the method could be used to measure the rates of the gaseous reactions of atomic hydrogen, This could not be done, however, because these reactions take place along such a short interval of the tube (5–20 cm.) that accurate results could not be expected. In the course of the preliminary experiments it was found, however, that if atomic hydrogen is led along a tube lined with a thin coating of sulfur, from $^1/_6$ to $^1/_5$ of the atomic hydrogen reacts to form hydrogen sulfide. This is to be expected since the first hydrogen sulfide formed rapidly catalyzes the recombination of the remainder of the hydrogen atoms.[6]

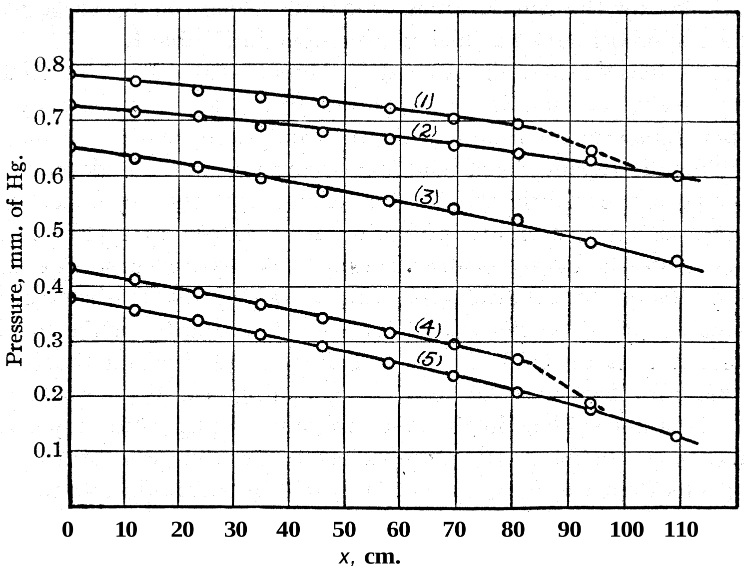

Fig. 5.—Curves 2, 3 and 5 obtained with discharge off and platinum out of outlet tube. Curves 1 and 4 obtained with discharge on and platinum at x = 83 cm.

It was also found that nitric oxide catalyzes the recombination without itself being reduced. Analysis of the gases leaving the mixing chamber showed that over 99% of the nitric oxide was unchanged. However, a very minute amount of ammonia was formed in each case. Thus in one experiment 2.8×10^{-5} mole of ammonia was found while there were available 0.01 mole of atomic hydrogen and 0.0088 mole of nitric oxide.

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[5] P. Harteck, Z. *physik. Chem.*, 139A, 98 (1928).

[6] Boehm and Bonhoeffer, *ibid.*, 119,385 (1926).

This ammonia may have been due to the presence of nitrogen oxide as an impurity in the nitric oxide. Blank experiments showed that it was not present in the original hydrogen or nitric oxide and that it did not come from the combination in the discharge of the hydrogen with a small contamination of nitrogen. It is difficult to explain the catalysis of nitric oxide by means of a chain mechanism such as has been used by Bonhoeffer for the similar effect of hydrogen sulfide, hydrochloric acid, etc., since if the nitric oxide molecule is ever broken up it is extremely unlikely to form again under the conditions of the experiment. Possibly an unstable molecule of the type H—NO is formed, in which case the mechanism would be

$$H + NO \longrightarrow H—NO$$
$$H—NO + H \longrightarrow H_2 + NO$$

The H—NO molecule might be quite short-lived and yet account for the effect.

The errors incident to this method of determining atomic hydrogen may be classified under four headings. In the first place the method is liable to the usual errors of calorimetry. These probably predominate in the present experiments, limiting the accuracy to 2–3%. Second, the method depends upon a knowledge of the heat of recombination of atomic hydrogen. This quantity, however, is now known with an accuracy within the above limits. Third, the heat effect registered in the calorimeter may be too small either because the recombination is not completely catalyzed by the platinum or because some of the heat is conducted away by the hydrogen stream. The first effect is extremely improbable since the rate of diffusion of atomic hydrogen under the conditions of the experiment is so high that a minute speck of metal in front of the calorimeter completely stops the heat effect. Further, in some of the preliminary experiments a thermometer with a silvered bulb was hung in the gas leaving the calorimeter and showed no temperature rise. Since the quantity of hydrogen flowing was small it would have had to be heated to an unreasonably high temperature to remove an appreciable amount of heat from the system. Finally, heat may be brought to the calorimeter in other ways than by the recombination of the atoms. Thus heat may be conducted from the discharge along the glass walls. This, however, was too small to affect the results since, when the whole discharge tube was water cooled, numerous runs in catalytically active apparatus showed no heat effect. This fact also removes the possibility of metastable molecules bringing energy to the calorimeter. It might also be supposed that, since the atomic hydrogen is recombining along the tube between the calorimeter and the discharge tube, sufficient heat could be liberated to affect the results. This is unlikely since in some of the preliminary experiments this tube was water cooled without affecting the results.

The accuracy of the method, therefore, is limited by the errors involved in the calorimetry of quantities of heat which, in this case, varied from 5 to 40 Cal. per minute.

The Three-Body Mechanism

It will now be shown that the results summarized in Table I are in accord with the predicted mechanism of recombination by triple impacts. The fundamental assumption is that at constant pressure

$$\frac{-\mathrm{d}N_\mathrm{H}}{\mathrm{d}t} = 2\Sigma\nu_3 \tag{2}$$

where N_H is the number of hydrogen atoms per cc. at the time t and $\Sigma\nu_3$ is the number of triple impacts per second per cc. in which at least two of the colliding bodies are hydrogen atoms.

There is considerable uncertainty as to the quantitative definition of a three-body collision. Whatever be the definition, however, $\Sigma\nu_3$ may be set equal to

$$\Sigma\nu_3 = K_1N_\mathrm{H}^2 + K_2N_\mathrm{H}^3 + K_3N_\mathrm{H}^2N_{\mathrm{H}_2} \tag{3}$$

where K_1, K_2 and K_3 are proportionality constants and N_{H_2} is the number of hydrogen molecules per cc. The first term on the right of Equation 3 takes account of triple imparts in which the wall is the third body. In the second term the third body is a hydrogen atom and in the third a hydrogen molecule.

To express the present results it will be necessary to take account of the fact that the atomic hydrogen is recombining at variable pressure while flowing along the tube. This may be accomplished by writing the equation of continuity of the hydrogen atoms

$$\frac{\partial N_\mathrm{H}}{\partial t} - \frac{\partial(N_\mathrm{H}u)}{\partial x} = 0 \tag{4}$$

where u is the linear velocity of the gas at the point x

$$u = \frac{n}{\pi r^2\left(N_{\mathrm{H}_2} + \frac{1}{2}N_\mathrm{H}\right)} \tag{5}$$

Here n is the number of hydrogen molecules admitted to the apparatus per second ($n = n_0N_A$). Since

$$N_\mathrm{H} + N_{\mathrm{H}_2} = \frac{P}{kT} \tag{6}$$

and

$$\alpha = \frac{N_\mathrm{H}}{2N_{\mathrm{H}_2} + N_\mathrm{H}} \tag{7}$$

$$N_\mathrm{H} = \frac{P}{kT} \times \frac{2\alpha}{1+\alpha} \tag{8}$$

$$N_{\mathrm{H}_2} = \frac{P}{kT} \times \frac{1-\alpha}{1+\alpha} \tag{9}$$

Substituting Equations 2, 3, 5, 8 and 9 in Equation 4, there is obtained

$$\frac{-\partial\alpha}{\partial x} = \frac{\pi r^2}{n} \times K_1 \frac{4\alpha^2 P^2}{(1+\alpha)^2 k^2T^2} + K_2 \frac{8\alpha^3 P^3}{(1+\alpha)^3 k^3T^3} + K_3 \frac{4\alpha^2(1-\alpha)P^3}{(1+\alpha)^3 k^3T^3} \tag{10}$$

Equation 10 cannot be integrated except by means of a series development. It is possible, however, that any one of the three terms may predominate. To integrate these three simplified equations it will be necessary to know P as a function of x. This pressure gradient could be calculated from the data of Harteck[5] but this would make the computations quite complicated. Since Harteck found that the viscosity of mixtures of atomic and molecular hydrogen does not differ greatly from the value for molecular hydrogen alone, it is believed that an empirical method will be sufficiently accurate for the present purposes. It will therefore be assumed that

$$P = \sqrt{P_0^2 - \beta x} \tag{11}$$

where β is a constant to be evaluated from the data of each experiment. This equation is equivalent to the assumption that the viscosity of the gas is constant along the tube. In order to calculate the constant β it may reasonably be assumed that, since all of the hydrogen is molecular after leaving the calorimeter, the curves of Fig. 5 give the true pressure gradient for this part of the flow. If this is the case it is possible to determine the pressure P at the calorimeter from the measured value of P_1, by interpolation. Since P, P_0 and x are known, β may be calculated for each run. Although this method of calculation is approximate, the results seem fairly certain for large values of x. Thus in the first five of the runs calculated in Table II β varies irregularly between 3520 and 4440 (pressure expressed in dynes/cm.^{2}). In the last five runs β decreases fairly regularly from 4160 to 3190. The calculated value of β for molecular hydrogen is 3570.

Using the assumption of Equation 11 and setting alternately K_2 and K_3, K_1 and K_3, K_1 and K_2 equal to zero, the following equations are obtained

$$K_1 = \frac{nk^2T^2\left[\frac{1}{\alpha} - \frac{1}{\alpha_0} + 2\ln\frac{\alpha_0}{\alpha} + \alpha_0 - \alpha\right]}{4\pi r^2\left(P_0^2x - \frac{\beta x^2}{2}\right)} \tag{12}$$

$$K_2 = \frac{5\beta nk^3T^3\left[\frac{1}{2}\left(\frac{1}{\alpha^2} - \frac{1}{\alpha_0^2}\right) + 3\left(\frac{1}{\alpha} - \frac{1}{\alpha_0}\right) + 3\ln\frac{\alpha_0}{\alpha} + \alpha_0 - \alpha\right]}{16\pi r^2[P_0^5 - (P_0^2 - \beta x)^{5/2}]} \tag{13}$$

$$K_3 = \frac{5\beta nk^3T^3\left[4\ln\frac{\alpha_0}{\alpha} + 8\ln\frac{1-\alpha}{1-\alpha_0} + \frac{1}{\alpha} - \frac{1}{\alpha_0} - (\alpha_0 - \alpha)\right]}{8\pi r^2[P_0^5 - (P_0^2 - \beta x)^{5/2}]} \tag{14}$$

Equation 12 embodies the assumption that the recombination of hydrogen atoms is largely heterogeneous; Equation 13 that it is homogeneous, but that only the hydrogen atoms can act as the third body; and the last equation that only the hydrogen molecule can act as the third body. Table II summarizes the values of these constants calculated from some of the experiments of Table I. The values of α_0 used in the calculations were taken from the extrapolated curve of Fig. 4.

TABLE II

SUMMARIZED VALUES OF CONSTANTS

P_0	x	α_0	α	$K_1 \times 10^{16}$	$K_2 \times 10^{32}$	$K_3 \times 10^{32}$
0.508	86.2	0.810	0.475	4.20	4.20	12.40
.584	86.2	.790	.350	4.24	3.60	9.04
.632	86.2	.778	.290	4.68	4.16	8.24
.714	86.2	.758	.202	5.04	4.72	6.32
.798	86.2	.740	.151	5.20	4.96	4.84
.508	65.9	.810	.534	3.84	3.48	14.44
.642	65.9	.775	.380	3.76	2.84	7.44
.716	65.9	.758	.282	4.24	3.24	6.04
.788	65.9	.743	.217	4.44	3.48	4.88
.874	65.9	.728	.170	5.12	3.60	3.88

Each of the three constants shows a well-defined drift so that it may be concluded that none of the three equations expresses the actual mechanism of recombination. The variation of the constants, however, is such as to make it seem probable that the differential Equation 10 does express the correct mechanism. Thus as the pressure is increased the apparent value of K_1 increases, K_2 first decreases and then increases and K_3 decreases. The increase in K_1 indicates that there is relatively less recombination taking place on the wall at the high pressures. Similarly, the decrease of K_3 shows that there are relatively more effective collisions involving two hydrogen atoms and one hydrogen molecule at the higher pressures. These two effects combined can account for the changes in K_2. Thus increasing the pressure lessens the relative amount of wall reaction, which would cause K_2 to decrease, and increases the relative amount of recombination caused by the molecules, which would cause K_2 to increase. Since the wall reaction varies as the square of the pressure and the "molecule reaction" as the pressure cubed, the first effect predominates at the low pressures and the second at the higher pressures. K_2, therefore, passes through a minimum.

An attempt was made to calculate the constants directly from the differential equation, by obtaining the slope graphically. This is a very unfavorable way of calculating the data since the determinants of the various sets of equations nearly vanish. Thus a change of 2% in the slope changes the constants by a factor of 100 or more.

A series of approximate calculations, however, indicated that the data would be satisfied if K_1, K_2 and K_3 are of the orders of magnitude 10^{-16}, 10^{-32} and 10^{-32}, respectively.

The approximate values of the constants so obtained may render possible a more quantitative definition of a three-body collision. Thus a three-body collision in which the wall is the third body may be defined as a collision between two hydrogen atoms occurring less than a short distance, 6, from the wall. In other words, the number of such collisions per second per cc. equals the number of collisions between hydrogen atoms per sec. per cc. times the volume of a cylindrical shell of radius r, thickness δ and length such that the volume inclosed by the shell shall be 1 cc. That is

$$\nu_{3(\text{wall})} = 2N_{\text{H}}^2\sigma_{\text{H}}^2\sqrt{\frac{\pi kT}{m_{\text{H}}}} \times \frac{2\delta}{r} \tag{15}$$

where σ_{H} is the diameter and m_{H} the mass of the hydrogen atom. Therefore

$$K_1 = \frac{4\sigma_{\text{H}}^2\delta}{r}\sqrt{\frac{\pi kT}{m_{\text{H}}}} \tag{16}$$

In arriving at this relation it is assumed that the tube wall is perfectly smooth. Although this cannot be the case, the actual area of the wall is probably not greatly different from the assumed value since the small adsorbing pores of the wall are filled with water. Substitution of numerical values in Equation 16 shows that 6 is of the order of magnitude of 10^{-7} cm. Irregularities in the wall would decrease this figure. In the calculation the diameter of the hydrogen atom has been assumed to be 2×10^{-8} cm.

A three-body collision involving three molecules may be defined in a number of different ways. For example, Tolman[7] defines it as one in which the distances between Molecule I and Molecule II and between Molecule II and Molecule III are equal to or less than some short distance, 6. From the relation obtained by him it follows that

$$K_2 = 32\pi^2\sigma_{\text{H}}^4\delta\sqrt{\frac{kT}{\pi m_{\text{H}}}} \tag{17}$$

and

$$K_3 = 16\pi^2\sigma_{\text{H}}^2\left(\frac{\sigma_{\text{H}} + \sigma_{\text{H}_2}}{2}\right)^2\delta\sqrt{\frac{kT}{\pi m_{\text{H}}}}\left(1 + \sqrt{\frac{m_{\text{H}} + m_{\text{H}_2}}{m_{\text{H}_2}}}\right) \tag{18}$$

where σ_{H_2} and m_{H_2} are, respectively, the diameter and mass of the hydrogen molecule. From either equation it is found that 6 is of the order of magnitude 10^{-9} cm.

The definition suggested by Herzfeld[1] and used by Bodenstein[S] in his calculations of the rate of the reaction between NO and O_2 is identical with the above except that 6 is identified as the diameter of the colliding molecules. The expressions obtained from the two definitions for the number of triple collisions differ only by a numerical factor of the order ten.

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[7] Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," The Chemical Catalog Co., New York, 1927, p. **247.**

[8] Bodenstein, Z. *physik. Chem.*, **100,** 68 (1922).

Syrkin[9] has calculated the number of multiple collisions between point molecules by defining a multiple collision as one in which the colliding molecules are within a small sphere of radius r. Applying his general equation to the present case, there are obtained the equations

$$K_2 = \frac{\left(\frac{4}{3}\pi r^3\right)^2}{3!r} \times \frac{2}{3}\sqrt{\frac{2\pi kT}{m_H}} \tag{19}$$

$$K_3 = \frac{\left(\frac{4}{3}\pi r^3\right)^2}{2!r} \times \frac{2}{3}\sqrt{2\pi kT}\sqrt{\frac{\frac{2}{m_H} + \frac{1}{m_{H_2}}}{3}} \tag{20}$$

From either equation r is found to be of the order 10^{-8} cm.

It may therefore be concluded that the recombination of hydrogen atoms proceeds according to the predicted three-body mechanism. The experimental proof, however, is not as definite as might be desired since no integral of Equation 10 was obtained. For this reason the experimental method was not considered suitable for an investigation of the effect of mixing other gases with the dissociated hydrogen.

There are a number of other possible mechanisms for the recombination of atomic hydrogen. Thus it might be supposed that even under the best circumstances the walls of the containing vessel still exert a specific catalytic power at relatively isolated points. If, however, this were the principal means of recombination, K_1 calculated from Equation 12 should be constant. It might further be supposed that the water vapor present in the gas might enter into the mechanism. The fact that Bonhoeffer[10] and Mohler[11] have shown that the OH bands are excited by atomic hydrogen might be cited as evidence in favor of this statement. Since, however, the reaction

$$H + H_2O \longrightarrow H_2 + OH - 12 \text{ Cal.}$$

is endothermic, it may be ruled out. It seems more probable that unexcited OH molecules are produced in the discharge tube and that the bands result from triple impacts between these and two hydrogen atoms. Under the conditions of the present measurements such an effect would be too small to influence the results.

No account has been taken of the possibility of recombination taking place in the adsorbed phase. Langmuir[12] has shown that atomic hydrogen is appreciably adsorbed by glass surfaces at room temperature but in his experiments the glass was thoroughly baked out prior to the adsorption while in the present case the tube wall was covered with a film of water. Furthermore, if the wall were covered with a reactive adsorbed film the

[9] Syrkin, *Physik. Z.*, 24, 236 (1923).

[10] Bonhoeffer, *Z. physik. Chem.*, 116, 391 (1925).

[11] Mohler, *Phys. Rev.*, 29, 419 (1927).

[12] I. Langmuir, THIS JOURNAL, 34, 1310 (1912); 36, 1711 (1914); 37, 417 (1915); 38, 2270 (1916).

recombination would be at least 10^5 times more rapid. In the light of these facts it seems extremely improbable that the wall as a whole adsorbs atomic hydrogen. There remains the possibility that isolated points on the wall are absorbent and hence catalytic. Such a possibility is unlikely since if this were the case duplicate results could not be obtained in different apparatus.

In conclusion the author wishes to express his indebtedness to Dr. H. C. Urey and to Professor K. F. Herzfeid for their advice during the course of this work.

Summary

1. A calorimetric method for the estimation of the amount of atomic hydrogen obtained from a Wood tube is described, together with the application of this method to the measurement of the rate of recombination of the hydrogen atoms.
2. This rate has been measured through the pressure range 0.5–0.9 mm. of mercury.
3. It was found that, under the conditions of the experiment, one-fifth to one-sixth of the atomic hydrogen present reacted with solid sulfur and that nitric oxide catalyzes the recombination of the atomic hydrogen.
4. The data obtained for the rate of recombination are discussed and it is concluded that they are in accordance with the predicted three-body mechanism.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE REACTIVITY OF IODINE CYANIDE IN DIFFERENT ORGANIC SOLVENTS

BY ERWIN CHARGAFF[1]

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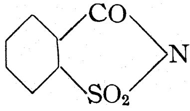
F. Feigl and the author have stated[2] that the reactivity of iodine toward the silver salt of saccharin depends upon the solvent used. In the so-called active solvents, which give brown solutions of iodine (*viz.*, ethyl ether, ethyl alcohol, etc.), almost only AgI is formed. In the inactive solvents (*viz.*, carbon disulfide, carbon tetrachloride, etc.), in which iodine dissolves with a violet color, there apparently is formed an addition compound 

$NAg...I_2$, which, being unstable, easily decomposes into

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[1] Milton Campbell Research Fellow in Chemistry, 1928–1929.

[2] F. Feigl and E. Chargaff, Monatsh., 49,417 (1928). (In. C. *A*., 22, 3816 (1928), and 22, 4083 (1928), both times the second author's name is incorrectly reported.)

silver saccharate and iodine. This remarkable difference in reactivity is attributed by the authors to the fact that in the brown solutions the iodine is present in a molecular compound with the solvent, whereas in the violet solutions we are dealing with uncombined molecules of iodine. The absorption spectra of these violet solutions are almost identical with that of iodine vapor. Therefore it was of some interest to compare the reactivity of an interhalogen compound with that of iodine in the same solvents. For this purpose the reaction of silver saccharate in solutions of iodine cyanide with different solvents has been investigated under identical conditions.

Experimental Part

The silver saccharate used was prepared by adding a boiling aqueous solution of 8 g. of silver nitrate to a boiling solution of 10 g. of sodium saccharate The precipitate was washed with water, acetone and ether. By analysis it was shown to be pure silver saccharate. The best method for preparing iodine cyanide proved to be that recommended by V. Grignard and P. Crouzier,[3] which consists in passing a stream of chlorine through a solution of iodine in aqueous sodium cyanide, and subsequently removing the iodine cyanide by extraction with ether. In order to obtain a good yield of the cyanide it was found to be desirable to remove the ether by distillation in a vacuum at room temperature and not on a steam-bath, as iodine cyanide is very volatile even below 40°. Out of the highly concentrated ether solution the iodine cyanide is then precipitated by adding carbon tetrachloride. The product thus obtained is almost pure (m. p. 145.5° instead of 146.5'). For ordinary purposes the very unpleasant sublimation thus may be avoided. However, for the experiments given here the original product was slowly sublimed in small portions at 40°, whereupon the melting point rose to 146° in the closed capillary tube. From 31.5 g. of iodine 35.2 g. of iodine cyanide was obtained (92.6% of the iodine used). The solvents were all freshly distilled and dried. The carbon disulfide was shaken with mercury and calcium chloride and then distilled.[4]

In all cases the reactions were carried out by refluxing 0.6 g. of silver saccharate with solutions of 0.8 g. of iodine cyanide in 80 cc. of the respective solvents for two hours. Longer heating does not change the results. When still hot the solution then was decanted from the silver salt and the latter heated with fresh solvent several times until a sample of the solvent did not liberate iodine from a potassium iodide solution. To determine the silver in the reaction product the previous method of analysis could not be employed. A method was necessary which allowed the determination of silver iodide and at the same time of the amount of silver cyanide which may have been formed. Therefore, each time a weighed sample of the product was heated with dilute nitric acid and the liquid separated from the silver iodide and silver cyanide with a filter crucible. In the filtrate the amount of silver, which came from unchanged silver saccharate, was determined by titration with 0.1 *N* ammonium thiocyanate solution after the method of Volhard. The residue in the crucible was washed with warm aqueous ammonia after weighing and the loss of weight indicated the amount of silver cyanide dissolved by the ammonia. However, as the amounts of silver iodide and silver cyanide insoluble in nitric acid were very slight, great accuracy

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[3] Grignard and Crouzier, Bull. *soc. chim.*, [4] **29,** 214 (1921).

[4] Th. Sidot, *Compt. rend.*, **69,** 1303 (1869); H. Arctowski, *Z. anorg. Chem.*, 6, 255 (1894); M. v. Unruh, *ibid.*, 32, 407 (1902).

could not be expected for the determination of the silver cyanide. Some of the results obtained are given in Table I.

Table I

Results of Experiments

Solvent	Digest, hours	Silver salt, *g.*	Insol. res, *g.*	Sol in NH_4OH, *g*	NHACN *N/10, cc.*	Silver saccharate recovered, *g.*	%
Abs. ether	2	0.2046	0.0007	....	7.02	0 2035	99.47
Ether	2	.3757	.0015	0.0004	12.89	.3737	99.46
Ether	5	.3215	.0016	0003	11.02	.3195	99.37
Abs. alc.	4	.2927	.0020	.0008	10 00	.2900	99.06
Abs. alc.	2	.3434	.0024	....	11.74	.3403	99.11
Benzene	4	.2772	.0009	....	9.52	.2760	99.56
Benzene	2	.3988	.0008	....	13.72	.3977	99.73
Carbon tet.	2	.2189	.0012	....	7 50	.2174	99.32
Chloroform	2	.3423	.0015	....	11.74	.3403	99.42
Carbon disulfide	4	.3158	.0022	.0009	10 81	.3134	99 24
Carbon disulfide	2	.3968	.0021	....	13.59	.3940	99.29

Discussion of the Results

The experiments described above gave the result that iodine cyanide does not act on silver saccharate at all, whereas iodine does, and there cannot be found any influence due to the nature of the solvent used. In Table II are recorded the respective amounts of silver iodide expressed as percentage of the reaction products in the cases of both iodine and iodine cyanide.

Table II

Silver Iodide Expressed as Percentages

	Abs. ether	Ether	Abs. alc.	Benzene	Chloroform	Carbon tetrachloride	Carbon disulfide	Pet. ether
Reaction with I_2	90.15	95.76	91.30	88.20	86 94	24.57	0	0
Reaction with ICN	0.53	0.59	092	0.36	0.58	068	0.74	..

In the reaction with iodine there appears to be a decisive difference according to the use of an active or inactive solvent (with the exception only of chloroform and benzene),[5] while with iodine cyanide no influence of the solvent can be stated at all, the amount of silver iodide formed being very small in all cases. The statement of F. Ephraim[6] that the reactions of the interhalogen compounds are merely weakened reactions of the free halogens does not prove to be correct at least in this case. In order to explain these facts two assumptions could be made. Either it could be assumed that, contrary to the case of iodine, iodine cyanide does not give addition compounds with the active solvents and that to these addition compounds is due the formation of silver iodide in brown solutions of iodine, or (and this may be the more plausible explanation) that iodine cyanide—and perhaps other interhalogen compounds, too—

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[5] F. Feigl and E. Chargaff, ref. 2, pp. 418 f.

[6] F. Ephraim, "Anorganische Chemie," 2d and 3d ed., p. 300.

does not function as a "mixed halogen," but as a salt of hydrocyanic acid with the weak base iodine hydroxide.[7] The salt-like behavior of the iodine-halogen compounds is emphasized by several investigators.[8] In conclusion it may be said that according to the results which have been obtained the hypothesis that the structure of the iodine cyanide molecule is different from that of the iodine molecule is confirmed, and that it is to the different chemical nature of iodine cyanide that we may attribute its divergent reactivity.

Summary

The reactivity of iodine cyanide toward silver saccharate in various solvents has been investigated. It is shown that contrary to the behavior of iodine the reactivity of iodine cyanide is independent of the nature of the solvent. From this fact the conclusion may be drawn that iodine cyanide represents a heteropolar compound and does not function as a "mixed halogen." The yield of iodine cyanide has been increased by modifying the purification methods.

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[Contribution from the Chemical Laboratory of the University of Utah]

THE DENSITIES OF COEXISTING LIQUID AND GASEOUS NITROUS OXIDE

By Elton L. Quinn and Grant Wernimont

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During an investigation of the internal pressure of liquid nitrous oxide by the measurement of its surface tension, the authors found that no data existed on the densities of the liquid and its saturated vapor at temperatures below zero. As these data were necessary for calculating the surface tension, it became necessary to interrupt the investigation and to attempt a set of measurements for supplying these values. This paper describes the method of making these determinations and the results obtained over a temperature range from 30 to $-50°$.

The densities of liquid nitrous oxide and its saturated vapor were determined between the temperatures of 30 and 0° by Villard[1] in the year 1894. While the reliability of these determinations has never been questioned, the temperature range covered is not great enough for the work at hand. The advisability of extrapolating these values to the lower temperatures was carefully considered but it seemed best under the circumstances to make direct measurements.

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[7] Cf. Abegg, "Handbuch der anorganischen Chemie," 1913, Vol. IV, 2, pp. 455 ff.

[8] P. Walden, *Z. physik. Chem.*, 43, 385 (1903); R. Abegg, *Z. anorg. Chem.*, 39, 330 (1904).

[1] Villard, *Compt. rend.*, 118, 1096 (1894).

As it was necessary to make measurements below the freezing point of mercury the usual method in which mercury is used as a confining liquid could not be used. The method of Young[2] seemed to be the only one applicable under these conditions and after slight modification was found to give quite satisfactory results. Several glass tubes of different lengths were filled to about two-thirds of their capacity with liquid nitrous oxide; the volumes of the liquid and saturated vapor were determined at different temperatures and the weight of the compound in each tube was measured. From these values by means of simultaneous equations it was possible to calculate the densities of the two phases at each temperature at which measurements were made.

Experimental Method

The five pycnometers used in this work were simple straight "soda-glass" tubes having an outside diameter of 12 mm. and a wall thickness of 2 mm. These tubes varied in length from 10 to 20 cm. and were graduated on the outside in mm. divisions. The greatest care was necessary in their manufacture as it was necessary for them to withstand at times a gas pressure as high as 68 atmospheres. It was found that proper annealing after working in the gas flame was much more important than the thickness of the tube wall, provided, of course, that it had a reasonable thickness. The two-thirds capacity filling of the tubes was also important because tubes having very much less than this amount could not be used over the whole temperature range. Stewart[3] showed in the case of carbon dioxide, which behaves much the same as nitrous oxide, that the liquid in a tube filled to less than about two-thirds of its volume contracts on cooling until some temperature is eventually reached where the liquid condensed from the gaseous phase, due to the lowering of the temperature, is equal to the contraction of the liquid phase. It is quite obvious that measurements made under such conditions would be of no value for density determinations.

The nitrous oxide used in this investigation was taken from a commercial cylinder of the liquefied gas manufactured by the Ohio Chemical and Manufacturing Company. The gas was carefully analyzed qualitatively using the tests suggested by Hackh[4] and found to be free from other oxides of nitrogen, halogens, carbon dioxide, sulfur compounds and ammonia. A small quantity of air was present but the most troublesome impurity was water vapor. In order to remove these impurities as well as any other substance that might be present in small amounts the liquid was fractionally distilled several times in an apparatus represented by the drawing in Fig. 1. The pycnometer, e, was cemented to the exit tube with de Khotinsky cement and the whole apparatus evacuated with an oil pump until the pressure was less than 3 mm., as indicated by a mercury manometer. During the evacuation the pycnometer was heated with a hand blast lamp until it was much too hot to permit touching with the bare hand. Nitrous oxide was then admitted to the apparatus and when the pressure reached that of the atmosphere the vacuum pump was stopped, the valve on the safety line closed and the safety valve adjusted. Then after a slight pressure had been put on the system, the valve to the safety line was opened and the pressure increased until the safety valve operated. While in this condition a Dewar flask containing solid carbon dioxide and ether, the temperature of which had been lowered to −100° by means of a vacuum

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[2] Young, *Trans. Chem. Soc.*, **59, 37, 126, 929 (1891)**; *Proc. Phys. Soc.*, **13,617 (1895).**

[3] Stewart, *Trans. Am. Soc. Mech. Eng.*, **30, 1111 (1908).**

[4] Hackh, **J. Am.** *Pharm. Assocn.*, *13, No.* **3,** March **(1924).**

pump, was pushed up over Tube a. Gaseous nitrous oxide was admitted from the cylinder fast enough to keep the safety valve close to the opening point until a sufficient quantity of the liquid had collected in Tube a. The supply of nitrous oxide was then cut off and the valve to the safety line closed. The freezing mixture was then transferred to Tube b and the liquid in a was permitted to distil into b, after which a Dewar flask containing liquid oxygen was substituted for the carbon dioxide freezing mixture. As soon as the nitrous oxide was frozen the vacuum pump was connected and the system evacuated to **3** mm. or less. As Tube b was cooled with liquid oxygen before all of the liquid in a had evaporated, a residue of liquid nitrous oxide was left in a which usually changed to a solid as soon as vapor pressure was decreased by lowering the temperature of Tube b. This residue was removed by heating after the vacuum pump had been operating for a few minutes. The residual gases were able to pass to the pump without coming in contact with the solid nitrous oxide. This procedure was repeated by distilling to a liquid in c and freezing to a solid and pumping in d and finally distilling the proper amount into the pycnometer e, freezing and evacuating. The pycnometer containing the proper amount of solid nitrous oxide was sealed while the vacuum pump held the pressure to less than **3** mm. and after the heated end of the tube had cooled it was removed from the liquid oxygen and the whole tube warmed slowly to room temperature. That this process was effective in removing the water from the gas is indicated by the fact that in preliminary experiments in which the gas was dried by passing it through a 50-cm. tower of calcium chloride, crystals of some impurity, supposedly water, separated from the liquid nitrous oxide on cooling to about —20°. Liquid nitrous oxide distilled in this apparatus failed to show such an impurity at any temperature. Weighing the tubes was delayed for several days so as to permit them to stand at room temperature long enough to give some assurance that they would not explode in the balance case. Several tubes exploded during this period, usually very soon after filling but none caused any trouble after starting the measurements, some even being heated to the critical temperature.

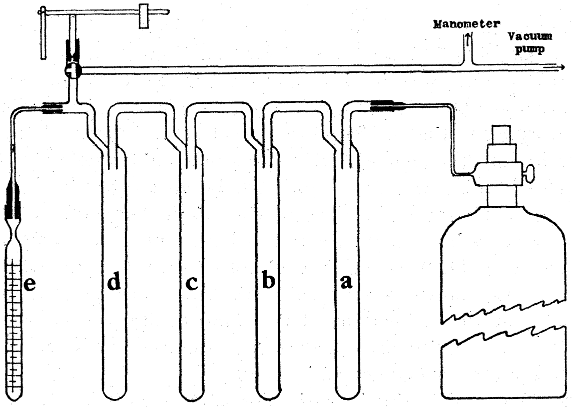

Fig. 1.

After weighing, the pycnometers were placed in long glass tubes having one end closed. A wad of cotton prevented the pycnometers from touching the bottom and a roll of paper held the top end securely in place. These tubes made it easy to handle the pycnometers and to clamp them in position in the thermostat. The thermostat used has already been described.[5] The temperature was kept constant by expanding

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[5] Quinn, THIS JOURNAL, 49, 2704 (1927).

liquid carbon dioxide through a cooling coil submerged in an alcohol-bath. Some improvement was made when a so-called "siphon cylinder" was substituted for the inverted carbon dioxide cylinder. This made handling easier and prevented water and oil from being forced through the coils. The temperature was adjusted every thirty seconds during the period of measuring and it was not difficult to hold it within ±0.25° of the desired temperature down to −60°. Temperature measurements were made with a pentane thermometer which had been calibrated twice by the U. S. Bureau of Standards. The last calibration was made during the summer of 1928.

The routine procedure of reading the volumes of liquid in the several tubes was as follows. The tubes were submerged in the alcohol-bath at the desired temperature for ten minutes. They were then removed and quickly shaken thoroughly and returned to the bath. At the end of six to seven minutes a reading was taken of the position of the meniscus on the tube graduations and it was again removed, quickly inverted and returned to the bath. In three to four minutes or as soon as the liquid nitrous oxide had drained from the sides of the tubes a second reading was made and if the two readings checked this value was used as the volume of the liquid at that temperature. The time necessary to reach equilibrium in the tube was determined several times by taking readings every twenty seconds until they became constant. It never took over seven minutes to reach this point.

After the readings had been completed the temperature of the tube was lowered in a solid carbon dioxide and ether bath and a small hole made in the tip of the pycnometer with a hand blast lamp. The tubes were then removed and the nitrous oxide permitted to escape. The last of this compound was removed with a vacuum pump and its place taken by air, the weight of which was easily determined. The weight of the tube was then determined, after which it was filled to the top with freshly boiled distilled water and again weighed. From these weighings and the temperature of the water the total volume of the pycnometer was determined. The top of the tube was then removed and the lower portion calibrated by filling with water to the marks reached by the liquid nitrous oxide at the various temperatures. The curvature of the meniscus in the case of water was, of course, different from that of the nitrous oxide and a correction for this difference had to be applied at each temperature.

The weight of the water in the meniscus was found in the following manner. A tube of the same size as that used for the pycnometers partly was filled with mercury and a little water placed on top. It was then put in a projection lantern and its image, enlarged 23 times, was projected on a white piece of paper. A drawing was made of the two menisci which is represented by Fig. 2, abcd being the meniscus of the water and efgh that of the mercury. These areas were then cut from the paper and weighed. The weight of abcd divided by the weight of abcd + efgh times 100 gave the percentage of the total area due to water above the line bc which was found in three determinations to be 62, 61 and 61%, respectively.

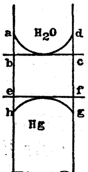

Fig. 2

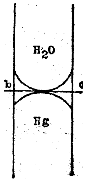

Fig. 3.

The same tube was dried and weighed with mercury, after which water was added and sucked out until the meniscus of the water just touched the meniscus of the mercury as in Fig. 3. The weight of the water was then determined and 61% of this was taken as the weight above the line bc. A tube containing liquid nitrous oxide was then warmed to 30° and a drawing made of its meniscus. The surface came so near to being flat that it was assumed that no appreciable error would be introduced by so considering it. An attempt was made to get a drawing of the nitrous oxide meniscus at a low temperature. This was unsuccessful and it was therefore necessary to be content with the apparent similarity of the meniscus of the liquefied gas at −60° and that of water at +30°. It was quite evident that if any correction was needed at this point it was very small. The correction at 30° was 0.05 g. This was the weight of the water in the curved meniscus above the comparatively flat surface of the liquid nitrous oxide. The correction at −60° was 0. By interpolation the correction to be subtracted at each temperature was determined.

The thermal expansion of the tube from −60° to the temperature at which the calibration was made was calculated and it was found that this made a difference in the volume of the tube of about 1 part in 500. As this correction was less than the probable error in the readings, it was not applied.

The dilation of a glass tube under a pressure practically the same as in this case was measured experimentally with liquid carbon dioxide[6] and was found to be less than 0.1%. This correction could, therefore, be neglected in these calculations.

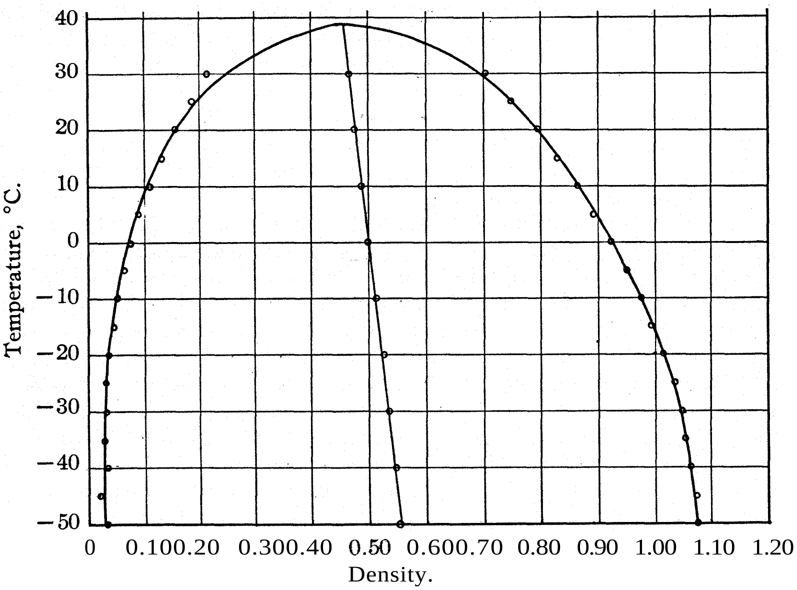

Fig. 4.

In order to eliminate as far as possible the experimental errors involved in determining the volume of the liquid nitrous oxide at the various temperatures, the volumes obtained by calibrating the tubes were plotted on coordinate paper 50 × 80 cm. and a curve was constructed for each set of readings. The agreement between the points on each curve was very satisfactory, only a few points failing to fall in the proper position. The values used for the calculations of the density of the liquid and the density of the gas were read from these curves. Tube No. 1 was discarded at the outset as it was quite evident that the volume of the liquid was too great to give reliable results for the gaseous density. Readings from Tube No. 3 also had to be discarded although the curve seemed to be quite regular. Apparently the trouble was due to an error in the total weight of the nitrous oxide or its total volume. As the tube had been cut it was quite

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[6] Quinn, THIS JOURNAL, 50, 675 (1928).

impossible to check back on either of these points. The densities were determined by setting up simultaneous equations between different sets of volume readings. Five calculations were thus made at each temperature and the values plotted in Fig. 4 were the averages between these results. In constructing this curve the value obtained by Villard for the critical temperature was used, that is, 38.8°. It is quite evident from an inspection of the curve that the values reported at times around 35° could not be used. The critical density was determined by the method of Cailletet and Mathias[7] in which the values for $(D + d)/2$ were plotted against the temperature and the straight line thus produced was extrapolated to the critical temperature. This gave a value of 0.459 for the critical density, while the value reported by Villard was 0.456.

Experimental Results

The results of these measurements are tabulated in Table I. Villard's results were plotted and values read from his curve at corresponding temperatures are given in the table for comparison. It will be noted that the agreement is, in general, very satisfactory. Lowry and Erickson[8] de-

TABLE I

THE DENSITIES OF COEXISTING LIQUID AND GASEOUS NITROUS OXIDE

	Quinn and Wernimont				Villard	
Temp., °C.	D Obs.	D Calcd.	d Obs.	d Calcd.	D	d
38.8	0.451	0.459	0.459	0.459	0.456	0.456
30	.704	.721	.217	.216	.680	.240
25	.750	.780	.181	.166	.740	.196
20	.793	.805	.153	.155	.784	.160
15	.826	.837	.133	.133	.820	.135
10	.861	.866	.111	.116	.856	.114
5	.894	.892	.090	.102	.886	.099
0	.925	.916	.073	.088	.912	.087
−5	.952	.939	.062	.077		
−10	.975	.960	.051	.066		
−15	.995	.980	.042	.058		
−20	1.013	.999	.038	.049		
−25	1.033	1.018	.030	.042		
−30	1.044	1.036	.029	.034		
−35	1.053	1 054	.028	.028		
−40	1 062	1 070	031	.022		
−45	1.071	1.087	.020	.017		
−50	1.079	1.103	.032	.013		

The experimental error for the liquid densities is estimated as about ±0.25%. The error of measurement of the gaseous phase is much greater. Neglecting the two highest and two lowest values, which are obviously much in error, the average deviation will run about ±2.0%.

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[7] Cailletet and Mathias, *Compt. rend.*, **102**, 1202 (1886); **104**, 1563 (1887).

[8] Lowry and Erickson, THIS JOURNAL, 49, 2731 (1927).

veloped equations for the relation between the values for $(D + d)/2$ and the densities of the gaseous and liquid phases of carbon dioxide. These equations when applied to nitrous oxide take the following form

$$D = 0.459 + 0.00111\,(t_k - t) + 0.1222\,\sqrt[3]{t_k - t}$$
$$d = 0.459 + 0.00111\,(t_k - t) - 0.1222\,\sqrt[3]{t_k - t} \quad \text{and}$$
$$(D + d)/2 = 0.459 + 0.00111\,(t_k - t)$$

In these equations D is the density of the liquid phase and d the density of the gaseous phase. The values of D and d calculated by means of these equations have also been tabulated and it will be noted that the agreement is not especially good and this disagreement is more pronounced at the higher temperatures. Lowry and Erickson, in the case of carbon dioxide, obtained excellent agreement between the calculated and observed values.

It is of some interest to use these results for calculating the molecular volume at absolute zero, using for this purpose the equation proposed by Sugden.[9] If the equation is written in the form $D - d = D_0(1 - T/T_K)^{3/10}$ D_0 being a constant which in the case of nitrous oxide has a value of 1,566, then the molecular volume at absolute zero would be 4411.566 or 28.1 ce. The actual volume occupied by each molecule could be calculated easily from this value by the use of Avogadro's number.

Summary

The densities of the coexisting gaseous and liquid phases of nitrous oxide have been determined over a temperature range of 80°. The critical density was found to be 0.459 and the molecular volume at absolute zero to be 28.1 cc. when calculated from Sugden's equation. The values for the density of the liquid and its saturated vapor show a very good agreement with those obtained over part of the temperature range by Villard.

SALT LAKE CITY, UTAH

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[9] **Sugden, J.** *Chem. Soc.*, 130, 1780 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

THE LEAD DIOXIDE–LEAD SULFATE ELECTRODE[1]

BY WARREN C. VOSBURGH AND D. NORMAN CRAIG

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Although the lead storage cell has been extensively studied from the practical side, the value of the lead dioxide–lead sulfate electrode, which is generally considered to form the positive electrode of the storage cell, is known only approximately. Gerke[2] gives **1.7** v. for the value of this electrode, the second figure being considered uncertain. This value is based on the work of Kendrick.[3] Vinal[4] has tabulated the values of different observers for the electromotive force of the lead storage cell. There is an average variation from the mean of 0.02 v. in the values for cells with the same acid concentration when all the results tabulated are considered.

In this investigation the electromotive force of the cell

$$\mathrm{Hg} \mid \mathrm{Hg_2SO_4}, \mathrm{PbSO_4}, \mathrm{H_2SO_4}\ (a = x) \mid \mathrm{H_2SO_4}\ (a = x), \mathrm{PbO_2}, \mathrm{PbSO_4} \mid (\mathrm{Pt}) \qquad (1)$$

was measured. The lead dioxide and lead sulfate were prepared chemically or, in the case of a few preparations of the former, by an electrolytic process different from that used in forming the positive plates of storage cells. From the electromotive force of Cell 1 the value of the lead dioxide–lead sulfate electrode was calculated.

By combining the electromotive force of Cell 1 with that of the cell[5]

$$\mathrm{Pb} \mid \mathrm{PbSO_4}, \mathrm{SO_4}^{--} \mid \mathrm{SO_4}^{--}, \mathrm{PbSO_4}, \mathrm{Hg_2SO_4} \mid \mathrm{Hg} \qquad (2)$$

the electromotive force of the cell

$$\mathrm{Pb} \mid \mathrm{PbSO_4}, \mathrm{H_2SO_4}\ (a = x) \mid \mathrm{H_2SO_4}\ (a = x), \mathrm{PbO_2}, \mathrm{PbSO_4} \mid (\mathrm{Pt}) \qquad (3)$$

was calculated.[6] This was found to agree as well as could be expected with the observed electromotive force of the lead storage cell.

Materials

Mercury.—Commercial redistilled mercury was purified by passing it repeatedly through a column of mercurous nitrate solution, and by fractionally redistilling it at least twice under reduced pressure in a current of air.

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[1] Condensed from a major portion of the dissertation submitted by D. Norman Craig to the faculty of the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Gerke, *Chem. Reviews*, 1, 390 (1925).

[3] Kendrick, *Z. Elektrochem.*, 7, 53 (1900).

[4] Vinal, "Storage Batteries," John Wiley and Sons, New York, **1924**, p. 166.

[5] (a) Henderson and Stegeman, THIS JOURNAL, **40**, 84 (1918); (b) Mellon and Henderson, *ibid.*, **42**, 676 (1920).

[6] The electromotive force of Cell **3** could not be measured directly on account of the difficulty of reproducing the lead sulfate–lead amalgam electrode when the electrolyte was a sulfuric acid solution. Lewis and Brighton, THIS JOURNAL, 30, 1908 (1917), have reported this difficulty, and their observations were confirmed in this investigation.

Lead Amalgam.—The lead amalgam was prepared electrolytically from purified mercury and twice recrystallized lead nitrate. It contained 10% of lead by weight.

Mercurous Sulfate.—The mercurous sulfate was prepared by adding at a slow rate a mercurous nitrate solution, made from twice recrystallized mercurous nitrate, to a hot 2 M sulfuric acid solution, which was made from C. P. acid. The precipitated mercurous sulfate was digested for nineteen hours on a steam-bath under 2 M sulfuric acid solution.[7]

Lead Nitrate.—Lead nitrate of C. P. quality was recrvstallized twice by the addition of concd. nitric acid to a hot concentrated solution of the salt. In the second recrystallization redistilled nitric acid and redistilled water were used.

Lead Sulfate.—Five hundred cc. each of a 0.5 M lead nitrate solution and 0.5 M sulfuric acid solution were added simultaneously drop by drop with constant stirring to 2 liters of boiling 0.1 M sulfuric acid solution. The lead sulfate was digested for twelve hours on a steam-bath under 2 M sulfuric acid solution.

Sulfuric Acid Solution.—The sulfuric acid solutions to be used as electrolytes in the cells were made by diluting concentrated C. P. acid to the required concentration with redistilled water.

The concentrations were determined by titrating a known weight of the solution with a standard carbonate-free sodium hydroxide solution. The latter was standardized by titrating in a similar manner a known weight of a hydrochlorioacid solution, which in turn had been standardized gravimetrically by the silver chloride method. Duplicate determinations agreed within one part in a thousand. The method of Randall and Scalione[8] was tried also as a check. Duplicate determinations did not agree quite so well, but the mean values agreed within an average of less than two parts in a thousand with the results of the first method. The concentrations given below are expressed in moles per 1000 g. of water.

Preparation of the Lead Dioxide

Several methods for the preparation of lead dioxide were tried because agreement of preparations made by different methods can be considered as evidence that the material is of sufficient purity and has a stable physical form.

Method 1.—Lead hydroxide was prepared by precipitation from a dilute lead nitrate solution by means of sodium hydroxide. It was well washed and then dissolved by means of sodium hydroxide solution. The resulting sodium plumbite solution was maintained at about 93°, stirred mechanically and bromine or sodium hypobromite solution added. It made little difference whether the oxidizing agent was bromine carried in by a current of air, bromine water or sodium hypobromite solution. In all cases the addition of the oxidizing agent was continued until the precipitate which was formed had turned dark brown or black.

Method 2.—The second method was similar to the first except that gaseous chlorine was used as the oxidizing agent. The chlorine was generated by the action of concd. hydrochloric acid on potassium permanganate and was washed by bubbling through water.

Method 3.—The third method consisted in hydrolyzing sodium plumbate. Lead dioxide was prepared by electrolysis and dissolved with hot concentrated sodium hydroxide solution. The solution was filtered and added drop by drop to a large volume of water kept at about 93° and mechanically stirred.

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[7] See Vosburgh and Eppley, THIS JOURNAL, 46, 110 (1924).

[8] Randall and Scalione, Met. *Chem. Eng.*, 13, 787 (1915).

Method 4.—Lead dioxide was also prepared by the electrolysis of a solution of 100 g. of lead nitrate and 400 cc. of concd. nitric acid in a total volume of three liters with a platinum gauze anode. The cathode was a platinum wire sealed into glass and was surrounded by a porous cup. The current density was kept in the vicinity of 2.5 amperes per square decimeter and the temperature was 93°.

A few preparations were made with the solution at room temperature. This material was not as satisfactory as that made at the higher temperature.

Lead dioxide was also deposited electrolytically directly on coils of platinum wire to be used later as cell electrodes. The electrolysis was carried out in hot solutions with various concentrations of lead nitrate and nitric acid and various current densities. Smooth as well as previously platinized wires were used. These electrodes were not satisfactory.

Other Methods.—Lead dioxide preparations made by hydrolyzing sodium plumbate with cold water and by oxidizing sodium plumbite with hydrogen peroxide were not satisfactory.

Digestion of the Lead Dioxide.—Two advantages may be gained by digesting lead dioxide with sulfuric acid at an elevated temperature. The lead dioxide may be brought to a more stable physical form[9] and any lead monoxide present may be converted to lead sulfate. Since lead sulfate was to be mixed with the lead dioxide in setting up the cells it was not an objectionable impurity.

The lead dioxide used in all but the preliminary experiments was digested under **3** M sulfuric acid solution on a steam-bath for several days. The color of the digested lead dioxide was nearly black, even in those cases in which the color was dark reddish-brown before digestion.

Apparatus

The electromotive forces were measured by means of a Leeds and Northrup Type K potentiometer, which was calibrated by the method described by the manufacturers.[10]

The standard cells were of the saturated type and were kept in an oil thermostat at 25°. They have been previously described.[11]

The experimental cells were kept in an oil thermostat. During the measurements at temperatures other than 25° two thermostats were used, one at 25° for the standards and the other containing the experimental cells. The temperatures were measured by a thermometer checked by the Bureau of Standards and are probably accurate to ±0.03°.

Preliminary Experiments

A number of separate lead dioxide–lead sulfate electrodes were set up in order to find out which methods of preparing lead dioxide gave the best results. They were combined, by means of an intermediate vessel containing some of the electrolyte, with two mercurous sulfate electrodes **and** the

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[9] (a) Vosburgh and Eppley, ref. 7, found that digestion of the mercurous sulfate with a sulfuric acid solution at boiling temperature helped in the preparation of reproducible Weston standard cells. The digestion probably brought the mercurous sulfate to a more stable physical form. See also (b) Cohen, "Physico-Chemical Metamorphosis and Some Problems in Piezochemistry," McGraw-Hill Book Co., Inc., New York, 1926, p. 50 and (c) Vosburgh, THIS JOURNAL, 50,2391 (1928).

[10] Leeds and Northrup Company, Bulletin No. **755,** 1923, p. *22.*

[11] Ref. 9 c, p. 2389.

resulting cells were measured at room temperature. The electrolyte was 0.1 M sulfuric acid solution throughout. The lead dioxide–lead sulfate electrodes were made by mixing lead dioxide and lead sulfate with the electrolyte and allowing this paste to flow around a coiled platinum wire in the electrode vessel. The platinum wire, which was 0.4 mm. in diameter (No. 26) and 4-cm. long, was sealed into a glass tube and connected with a copper wire terminal by means of mercury.

The preliminary experiments showed that different samples of undigested lead dioxide prepared by the same method gave cells differing by as much as 5 mv. Samples prepared by different methods gave cells differing by 10 to 15 mv. in some cases. When the lead dioxide was digested with a sulfuric acid solution on a steam-bath for several days, samples prepared by different methods gave cells agreeing within 2 mv. or better. The concentration of the sulfuric acid in which the lead dioxide was digested was of some influence. The best results were obtained when the acid concentration was from one to six molar. Nine-molar acid led to some erratic results. Therefore three-molar acid was used in digesting the lead dioxide for the final cells.

The preliminary experiments also led to the choice of Methods 1, 2, 3 and 4 described above as the best methods of preparing lead dioxide. When lead dioxide was deposited directly on the platinum coils by electrolysis, the resulting cells decreased in electromotive force steadily over periods of several weeks and were never observed to become constant.

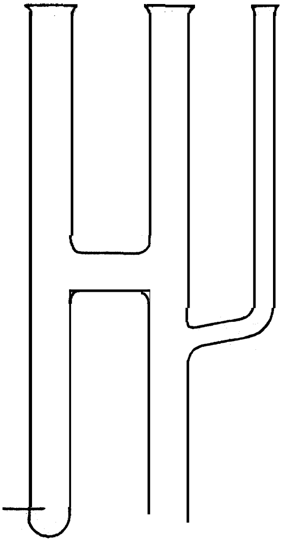

Fig. 1.—Cell vessel.

The Cell Hg | Hg_2SO_4, $PbSO_4$, H_2SO_4 | H_2SO_4, PbO_2, $PbSO_4$ | Pt

Preparation of the Cells.—The final cells were set up in vessels of the type shown in Fig. 1. The leg bearing the sealed-in platinum wire was used for the mercurous sulfate electrode and that with the side arm was used for the lead dioxide electrode. The sulfuric acid solutions used had been carefully standardized as described above. The lead dioxide had been digested in all cases.

In preparing some of the mercurous sulfate electrodes, air-free solutions were used. These had been standardized after freeing from air. Precautions were taken also to protect the mercurous sulfate from air by means of an atmosphere of carbon dioxide while the cell was being set up.[12] Others, as indicated in the tables below, were set up without protection from oxygen. Some lead sulfate was mixed with the mercurous sulfate paste and the layer of this mixture in the cell, at least 1 cm. deep, was covered with a layer of lead sulfate.

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[12] Vosburgh, This Journal, 47, 1258 (1925).

In setting up a lead dioxide–lead sulfate electrode, the tube bearing the platinum coil was first fixed in place. The glass tube was passed through a hole in a paraffined cork disk and the disk was pushed into the tube of the cell vessel for a distance of two or three centimeters. Melted beeswax was poured on top of the cork disk. Then a paste of about equal parts of lead sulfate and lead dioxide was introduced through the side arm. Enough was introduced to cover completely the platinum coil. This mixture was covered with a layer of lead sulfate. The opening of the vessel on the mercurous sulfate electrode side and the opening of the side arm were closed with paraffined cork disks pushed in for some distance and covered with a layer of beeswax. The finished cells were mounted on racks and connected as described by Vosburgh.[11]

Effect of Dissolved Oxygen.—Randall and Young,[13] whose paper appeared while this investigation was in progress, have shown that the presence of dissolved oxygen has an appreciable effect on the electromotive force of a calomel electrode with an acid electrolyte. Vosburgh[14] found that in setting up Weston standard cells protection from the air was of less importance when the electrolyte contained some sulfuric acid than when it was nearly neutral. Therefore, the effect of dissolved oxygen in the present cells is of interest. Table I gives a comparison of four cells prepared with and four prepared without precautions against dissolved oxygen.

TABLE I

EFFECT OF DISSOLVED OXYGEN

PbO_2	H_2SO_4, M	E.m f.[b] 1 day, v.	Change of e.m.f. 6 days, v.	2 wks., v.	4 wks, v.
1A	0.1000[a]	0.82587	0.13	0.23	....
2	.1000[a]	.82593	.06	.05	....
1A	.1035	.82874[c]	− .37	− .70	−0.85
2	.1035	.82833[c]	− .30	− .78	− .98

[a] Oxygen was excluded in the preparation of these cells by means of an atmosphere of nitrogen.

[b] Each value is the average value for two cells.

[c] On the basis of these values the value for a **0.1000** M electrolyte would be **0.82687** v.

The electromotive forces of cells made with oxygen present decreased, while the electromotive forces of the cells made in the absence of air[15] increased slightly but were more nearly constant than the others. The average initial electromotive forces of the two groups differed by about 1 mv. when that of the second group was calculated to an acid concentration of 0.1000 M. Tables II and III indicate that the presence of oxygen has a smaller effect on the constancy when the acid concentration is larger. In Table II a group of cells made without protection from the air and with 1.036 M acid as the electrolyte is compared with a group made with protection from the air and with an electrolyte of 1.964 M acid. In this table also each electromotive force value is an average of the values of duplicate cells.

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[13] Randall and Young, THIS JOURNAL, **50,993 (1928).**

[14] Ref. **12,** p. **1266.**

[15] Nitrogen was used rather than carbon dioxide in these cells.

TABLE II

EFFECT OF DISSOLVED OXYGEN. CONSTANCY

PbO$_2$	H$_2$SO$_4$ M	Electromotive force at 25°				
		2 wks., v.	5 wks., v.	7 wks., v.	12 wks., v.	16 wks., v.
1	1.036	.....	.....	0.95255	0.95253	0.95247
2	1.036	.....	.....	.95256	.95254	.95250
1	1.964[a]	1.00129	1.00132	1.00133	1.00126	
2	1.964[a]	1.00118	1.00123	1.00123	1.00120	

[a] Oxygen was excluded from the electrolyte of these cells.

The values of the electromotive forces were not measured at 25° previous to the measurements recorded in Table II. Measurements at higher temperatures indicated that the electromotive forces increased slowly during the first week or two. In the case of the last group of cells, at least, constancy was attained within two weeks and the electromotive forces remained constant for at least ten weeks. Table III will show that values for the cell with unit sulfuric acid activity calculated from the two groups agreed within 0.3 mv. It is to be concluded, therefore, that the effect of dissolved oxygen is largest in the cells with the most dilute electrolytes, and that it causes an uncertainty in the electromotive force of not more than 1 mv.

Electromotive Force.—The electromotive forces of all the cells set up were measured frequently over a period of several weeks. From the series of values so obtained the best value for the electromotive force was selected. In the case of the cells with the more dilute electrolytes from which oxygen was excluded, the initial values were taken as the best. In the case of cells with oxygen-free electrolytes in which the concentration was 1 M or larger, constancy was attained within a week or two after the cells were set up and the constant value was taken as the best one. For the other cells also the constant values were accepted as the best. Table III summarizes

TABLE III

CELL Hg | Hg$_2$SO$_4$, H$_2$SO$_4$ | H$_2$SO$_4$, PbO$_2$, PbSO$_4$ | (Pt)

H$_2$SO$_4$ *M*	Electromotive force at 25°					E°_{25}
	PbO$_2$ 1[b] v.	PbO$_2$ 2 v.	PbO$_2$ 3 v.	PbO$_2$ 4 v.	Av., v.	
0.05355[a]	0.7956	0.7954	....	....	0.7955	1.0580
.1000[a]	.8258	.8264	0.8264	0.8270	.8264	1.0577
.1035	.8287	.8283	....	....	.8285	1.0582
.2579[a]	.8747	....	....	....	.8747	1.0593
.5154	.9106	.9105	....	.9113	.9108	1.0597
1.036	.9526	.9526	....	....	.9526	1.0600
1.065[a]	.9550	....	.9551	.9550	.9550	1.0607
1.964[a]	1.0013	1.0012	....	....	1.0013	1.0597
2.206[a]	1.0121	....	....	....	1.0121	1.0590
3.409[a]	1.0638	1.0639	....	....	1.0639	1.0573

[a] Oxygen was excluded from the electrolytes of these cells.

[b] The numbers 1, 2, 3 and 4 refer to the method by which the lead dioxide was prepared.

the best electromotive force values for each acid molality and for lead dioxide prepared by the four different methods. Each value in the table is an average value for at least two cells, and in a few cases for four cells.

The different lead dioxide preparations gave cells agreeing within about 1 mv. at most, and in the case of the 1.065 M acid to within 0.1 mv. Commercial lead dioxide even after digestion gave cells with electromotive forces about 4 mv. higher than the others but of good reproducibility and constancy.

Cells with electrodes made by electrolytic deposition of lead dioxide on the platinum wire electrodes from hot solutions of lead nitrate agreed fairly well with each other, though not with the other cells, but were never satisfactory as to constancy. They showed a continuous decrease in electromotive force which did not come to an end during the two months' period of observation. Consequently their electrsmotive forces are not included in the table.

In the next to the last column of Table III is given the average value for each acid molality. From these the values of E° given in the last column were calculated by means of the equation

$$E^\circ = E + \frac{RT}{F} \ln \frac{a_{H_2O}}{4\gamma^3 m^3}$$

where m is the molality of sulfuric acid, γ is its activity coefficient and a_{H_2O} is the activity of the water. Values for the activity coefficients of sulfuric acid were obtained by graphic interpolation from the values of Lewis and Randall.[16] The values for the activity of water were calculated by the method described by Randall and Young.[17] The values so obtained agreed with corresponding values calculated from the vapor pressure data of Grollman and Frazer.[18]

The cells with the smallest acid concentrations were the least reproducible and the most variable when made with oxygen-free electrolytes. The E° values for these cells are therefore to be given less weight than the others. The activity coefficients of sulfuric acid have been less well established for the larger concentrations than for concentrations in the vicinity of 1 or 2 M. . Therefore, the last value may be considered questionable. The others give $E^\circ_{25} = 1.060 \pm 0.001$ v. as the best value for Cell 1.

The electromotive force of the cell

$$H_2\ (Pt)\ |\ H_2SO_4\ (a = 1)\ |\ H_2SO_4\ (a = 1),\ PbO_2,\ PbSO_4\ |\ (Pt) \qquad (4)$$

which on the basis of the usual conventions can be called the potential of the lead dioxide–lead sulfate electrode, can be calculated from the electromotive force of Cell 1 and that of the hydrogen–mercurous sulfate cell.

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[16] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book *Co.*, New York, 1923, p. 357.

[17] Ref. 13, p. 1002.

[18] Grollman and Frazer, THIS JOURNAL, 47, 712 (1925).

The electromotive force of the latter when the sulfuric acid electrolyte has unit activity is given by Gerke[19] as 0.6213 v. Therefore the electromotive force of Cell 4 at 25° is $E_{25}^{\circ} = 1.681 \pm 0.001$ v.

Temperature Coefficients

The electromotive forces of a number of representative cells were measured at five-degree intervals of temperature between 20 and 40°. The temperature was changed successively from 25 to 20, 30, 35, 40, 35, 30 and 25°. The cells were maintained at each temperature for a period of three or four days, except at 20° at which temperature they were kept for two days. Readings were taken at frequent intervals. The standards were kept at 25° in a separate bath. In general the cells showed no change greater than 0.01 mv. after the third day. The values given in Table IV are the averages for all cells with the same acid molality. The changes in the electromotive force of the individual cells with the same acid concentration showed an average variation from the mean of ±0.02 mv.

TABLE IV

CHANGE OF ELECTROMOTIVE FORCE WITH TEMPERATURE

H_2SO_4, M	No. of cells	E_{25}, v.	$E_t - E_{25}$, mv. 20°	30°	35"	40°	35°	30°	25°
0.1000	11	0.82617	$1.98	−1.92	−3.81	−5.69	−4.03	−2.02	−0.15
.5154	6	,91076"	....	....	....	−2.32	−1.57	−0.79	....
1.036	6	.95267	$0.30	−0.26	−0.47	−0.66	−0.47	−0.25	−0 00
1.964	4	1.00128"	....	....	....	....	+0.35	+0.18	....
3.499	4	1.06378[a]	....	....	....	....	+0.62	+0.34	....

[a] *These values at 25° are the values obtained after the series of temperature changes rather than before. In the first case (0.5154 M electrolyte) the cells appeared to be variable during the early part of the run, while in the other two cases the cells were set up only shortly before the second measurements at 35°.*

It is to be noted that the temperature coefficient varies with the molality of the electrolyte. It is negative in the cells with the most dilute electrolyte, passes through zero as the molality increases and becomes positive for cells with electrolytes having a molality larger than about 1.5 M.

The change of 0.15 mv. in the electromotive force of the cells with 0.1000 M electrolyte was permanent. Such a change might be expected in cells with dilute electrolytes. For cells with 1.036 M electrolyte the change in electromotive force with temperature as determined with rising temperature showed excellent agreement with corresponding values determined with decreasing temperature. These cells had apparently attained constancy at 25° before the temperature was changed. Furthermore, the electromotive forces returned to their original 25° values soon after the temperature was lowered and showed constancy for some time thereafter. Their temperature coefficients are probably the most reliable of all.

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[19] *Ref.* 2, p. *385*

The Lead Storage Cell

The electromotive force of Cell **3**

$$Pb \mid PbSO_4, H_2SO_4\ (a = 1) \mid H_2SO_4\ (a = 1), PbO_2, PbSO_4 \mid (Pt)$$

can be calculated by combining the electromotive forces of Cell 1, Cell 2 (with a lead amalgam electrode) and the cell[20]

$$Pb \mid Pb^{++} \mid Pb(Hg);\ E = 0.0057 + 0.000165\,(t - 25) \qquad (5)$$

For the cell with an electrolyte of unit activity the calculated electromotive force is $E^{\circ}_{25} = 1.060 + 0.9648 + 0.0057 = 2.0335$ v.

Cell *3* represents the lead storage cell according to the double sulfate theory[21] of the action of the storage cell. It would not, however, represent the action of the storage cell on the basis of the higher oxide theory of Féry.[22]

To facilitate comparison of the electromotive force of Cell **3** with that of the lead storage cell, the acid molalities were converted to specific gravities. Then electromotive force was plotted against the specific gravity of the electrolyte and electromotive forces for certain specific gravities were read from the graph. These electromotive forces are compared in Table V with the most concordant of the values compiled by Vinal[4] for the lead storage cell, and also with the values of Kendrick.[3]

TABLE V

COMPARISON OF THE ELECTROMOTIVE FORCE OF CELL 3 WITH THAT OF THE LEAD STORAGE CELL

Sp. gr. 25°/25°	1.040	1.050	1.100	1.150
Gladstone and Hibbert, v.	1.898	1 913	1 963	2.003
Kendrick, v.	1.890	1.905	1.957	2.000
Dolezalek, v.	...	1.906	1.965	2.010
Vinal and Altrup, v.	1.890	1.903	1.956	2.000
Cell **3**, v.	1.894	1.909	1.962	2.006

Cell **3** agrees with the storage cells measured by Gladstone and Hibbert,[23] Kendrick,[3] Dolezalek[24] and Vinal and Altrup[4] as well as could be expected. This agreement makes it probable that the lead storage cell is not essentially different from Cell **3** and supports the double sulfate theory of its action.

Activity of Sulfuric Acid

It was suggested above that the apparent decrease in E° for Cell 1 (Table III) for the most concentrated acid solutions might be explained by an error in the value of the activity. It is of interest to calculate the values

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[20] Ref. 2, p. 382.

[21] Originally proposed by Gladstone and Tribe, *Electrician*, 9, 612 (1882); see also ref. 4, p. 146.

[22] Féry, *Chimie et Industrie*, *17*, 909 (1927).

[23] Gladstone and Hibbert, *J. Inst. Elec. Eng.*, 21, 425 (1892).

[24] Dolezalek, "Theory of the Lead Accumulator," 1904, p. 55.

of the activity coefficients from the results for Cell 1 and compare them with the values of Lewis and Randall. This comparison is made in Table VI. Each value for the electromotive force represents the mean value for duplicate cells. The cells in question were all made from the same preparation of lead dioxide with the exception of those with the 1.065 M electrolyte. In this case the lead dioxide was prepared by the same method but at a later time. In the third column of the table the electromotive forces corrected to unit water activity are given. From these the values for the activity coefficient in the fourth column were calculated, the value $\gamma = 0.149$ for 1.036 M acid being obtained by graphic interpolation from the data of Lewis and Randall.[16]

There is a fairly large difference between the two sets of activity coefficients in the most dilute solutions and also in the most concentrated. In the former case the activity coefficients based on Cell 1 are of doubtful reliability on account of the lower degree of reproducibility of the cells with the most dilute electrolytes. The activity coefficient for the 3.5 M acid solution, however, should be reliable.

TABLE VI

ACTIVITY COEFFICIENTS OF SULFURIC ACID

H_2SO_4, M	E.m.f., Cell 3, v.	E.m.f., $a_{H_2O} = 1$, v.	γ, Cell 3	γ, L. and R
0.05355	0.7956	0.7956	0.380	0.390
.1000	.8258	.8258	.302	.313
.1035	.8287	.8287	.303	.309
.2579	.8747	.8745	.220	.222
.5154	.9106	.9101	.175	.176
1.036	.9526	.9516	(.149)	.149
1.065	.9550	.9539	.149	.148
1.964	1.0013	.9990	.145	.146
2.206	1.0121	1.0094	.148	.150
3.499	1.0638	1.0584	.176	.183

Thermochemical Data

From the value E = 0.9526 v. and the temperature coefficients given in Table IV for the cell with the 1.036 M electrolyte, the values for the free energy change, entropy change and heat of reaction for the reaction

$$PbO_2 + 2Hg + 2H_2SO_4\ (1.036\ M) \longrightarrow Hg_2SO_4 + PbSO_4 + 2H_2O$$

are found to be $\Delta F_{25} = -43{,}960$ Cal., $\Delta S_{25} = -2.58$ Cal. and $\Delta H_{25} = -44{,}730$ Cal.

The heat of reaction can be calculated from the following thermochemical data, which have been taken from "International Critical Tables," except as noted: heat of formation of lead dioxide, $\Delta H_{18} = -62{,}600$ Cal.; heat of formation of lead dioxide (Millar[25]), $\Delta H_{25} = -65{,}960$ Cal.; partial heat

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[25] Millar, THIS JOURNAL, 51, 212 (1929).

of formation of sulfuric acid in 1.036 M sulfuric acid solution,"[26] $\Delta H_{25} = -206{,}700$ Cal.; heat of formation of mercurous sulfate, $\Delta H_{18} = -171{,}580$ Cal.; heat of formation of lead sulfate, $\Delta H_{18} = -214{,}600$ Cal.; partial heat of formation of water in 1.036 M sulfuric acid solution, $\Delta H_{25} = -65{,}340$ Cal. Combining these to give the heat of reaction, using the value from "International Critical Tables" for the heat of formation of lead dioxide, gives $\Delta H = -46{,}860$ Cal. Using Millar's value for the heat of formation of lead dioxide, the heat of reaction is $\Delta H = -43{,}500$ Cal.

Summary

1. The conditions necessary for the preparation of reproducible lead dioxide–lead sulfate electrodes have been determined.

2. Cells of the type Hg | Hg_2SO_4, $PbSO_4$, H_2SO_4 (xM) | H_2SO_4 (xM), PbO_2, $PbSO_4$ | (Pt) have been set up and their electromotive forces have been measured over a period of seven to sixteen weeks at 25° and also at 20, 30, 35 and 40°.

3. From the results the following have been calculated: the value of E^{0}_{25}, the electrode potential of the lead dioxide–lead sulfate electrode, the activity coefficients of sulfuric acid at various molalities, the electromotive force of the lead storage cell and the free energy change, the entropy change and the heat of reaction for the reaction $PbO_2 + 2Hg + 2H_2SO_4 \longrightarrow PbSO_4 + Hg_2SO_4 + 2H_2O$. The last compares favorably with the value calculated from thermochemical data.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BRITISH COLUMBIA]

THE HEAT OF ADSORPTION OF OXYGEN ON CHARCOAL

BY MELVILLE J. MARSHALL AND HAROLD E. BRAMSTON-COOK

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Keyes and Marshall[1] found 73,000 calories per mole for the differential heat of adsorption of oxygen on activated charcoal for initial amounts of gas adsorbed. This heat dropped slowly as the concentration increased to about 0.15×10^{-4} moles per gram of charcoal. As the concentration increased beyond this value the heat of adsorption fell off rapidly to *a* practically constant value of about 4300 calories per mole.

The course of the curve of differential heat of adsorption against concentration of adsorbed gas at very small concentrations is of considerable theoretical interest, particularly from the point of view of the hypothesis that adjacent carbon atoms may vary greatly in adsorptive character.

[26] Interpolated with the help of data of Bronsted, *Z. physik. Chem.*, 68, 702 (1910), for the differential heat solution of sulfuric acid.

[1] Keyes and Marshall, THIS JOURNAL, 49, 156 (1927).

The earlier work,[1] while emphasizing the importance of obtaining adsorptive data at small concentrations, suffered from a limitation with respect to the amount of charcoal used in the measurements. In the present work ten times the amount of charcoal was employed, making it possible to follow the relation between the heat of adsorption and concentration to very much smaller concentrations than have previously been reported.

Apparatus.—The arrangement of the apparatus is shown in Fig. 1, and is similar in many respects to that of the earlier work.[1] The chief difference lies in the arrangement of the ice calorimeter, which was supported in a silvered Dewar flask, C, after the arrangement described by Griffiths.[2] The interior of the Dewar flask was rendered water-tight by a large rubber stopper through which the neck of the calorimeter passed.

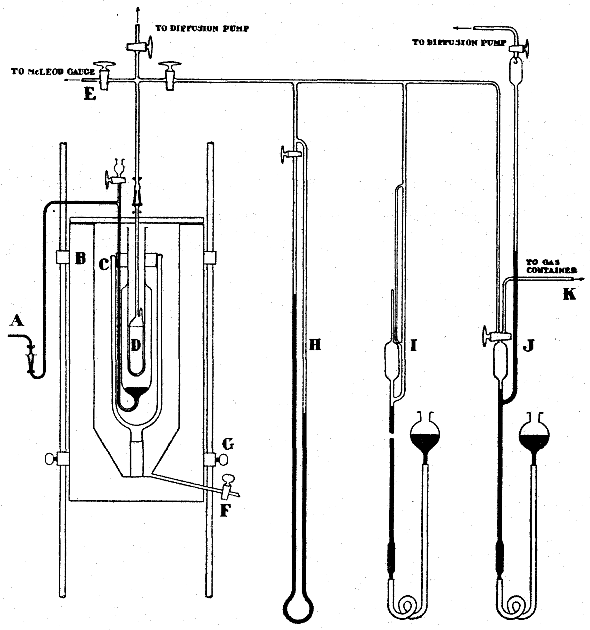

Fig. 1.

The Dewar flask was in turn supported inside the vessel B, which was provided with double walls, the space B being packed to the top with wool waste. The space C was filled with cracked ice and sufficient distilled water to fill the voids between the pieces of ice. This water did not quite reach the mouth of the calorimeter, which was closed with a thick piece of wool waste. The vessel B was covered with a piece of felt about 0.5 inch thick, which prevented a too rapid melting of the ice in C. As the ice melted, more was added every few hours, and the equivalent amount of water drained from F. The entire calorimeter could slide vertically and make contact with the fixed capillary tube at A in a manner similar to that described in the previous work.

The ice mantle was produced by the use of a mixture of solid carbon dioxide and ether contained in an open tube of slightly larger diameter than D. We found this

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[2] Griffiths, *Proc. Phys. Soc. London,* **36,** *1 (1913).*

method preferable, as the rate of freezing of the ice mantle could be easily controlled by dropping in small amounts of carbon dioxide at a time. The above arrangement of the ice calorimeter has the advantage that it can be operated for long periods of time. In the present investigation the ice mantle was found intact after being in continuous use for a week.

The oxygen was admitted to the apparatus from the gas pipet J, the bulb of which had a capacity of about 5 cc. The McLeod gage I had a low multiplying power of ten, and was used for intermediate pressures, while higher pressures were measured by the manometer H. A McLeod gage of ordinary size was connected at E for low pressure measurements when outgassing the charcoal.

The charcoal[3] used was a sample of activated coconut charcoal produced by the National Carbon Company It was washed in a Soxhlet extractor with hydrochloric acid and afterwards treated with hydrofluoric acid, the final ash content being 0.267%. Before use it was outgassed for about sixty hours at 1000°, using a platinum-wound resistance furnace. The outgassing was continued in every case down to a pressure of about 1×10^{-4} mm. After outgassing the charcoal weighed 25.792 g. During the preliminary outgassing the gas continued to come off for such long periods of time that interaction between the silica tube and the charcoal was considered possible. In the final measurements a lining of platinum foil was employed to prevent contact of the charcoal with the silica.

Experimental Procedure.—After outgassing the charcoal the calorimeter was raised into position until the quartz tube just touched the bottom of the inner tube. For the initial reading about 0.8 cc. of gas was admitted from the gas pipet. The position of the mercury thread was noted every ten minutes until the normal heat leak was resumed. Another increment of gas was added and the procedure repeated until about 250 to 300 cc. in all were added.

The data in the tables to follow give the oxygen added in moles per gram of charcoal, designated c. The quantity q is the total heat attending adsorption for the correspondingly tabulated values of c. To obtain these values of q allowance was made for the heat capacity of the gas admitted to the calorimeter, since the temperature of the former was in every case different from zero. Values of q were plotted against values of c and the slope $(\partial q)/(\partial c)$ was measured for various values of c. The quantity $(\partial q)/(\partial c)$ is the differential heat of adsorption per mole of oxygen at constant temperature, and is represented by Q. Data from two series of measurements are given in Table I. The corresponding values of Q, obtained by plotting the above p, c data suitably, are given in Table II.

The equilibrium pressures in Table I were originally measured for the purpose of correcting for unadsorbed gas in the calorimeter and connecting parts. As the low initial pressures gave negligible corrections they were not recorded. These initial pressures are, in fact, so low that they can be measured only by means of a specially sensitive McLeod gage. Such measurements are now being made in this Laboratory.

A marked discontinuity appeared in both Q–c curves at the point $c = 0.75 \times 10^{-4}$. Whether this is part of the phenomena or due to the method

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[3] The charcoal used previously was prepared from a sample of French gas mask charcoal. This latter charcoal was made from wood.

TABLE I

EXPERIMENTAL DATA

Press , mm.	$c \times 10^4$*	q	Press., mm.	$c \times 10^4$	
	Series 1			Series 2	
. .	0 0151	0 124	179 2	2 606	4.595
	.0361	272	271 5	3 488	4.999
. .	0793	558	382 2	4.599	5.436
	097	650		0 0136	0.119
	115	766		0405	.324
	151	1 009		0849	.647
	193	1 286		152	1.095
	232	1 542	0 05	222	1.575
	287	1 905	40	354	2.409
0 20	326	2 201	6 85	545	3.009
34	404	2 468	20 25	796	3.609
3.25	501	2 913	43 50	1 113	3.840
7.40	.611	3 247	128 2	2 153	4.472
14.73	.779	3 567	259 0	3 463	5.072
35.60	1 122	3 833	374 0	4 530	5.521
83.40	1 532	4.095	513 9	5 586	5.963
140.00	2 206	4 421			

TABLE II

VALUES OF Q

$c \times 10^4$	0.00	0.01	0.02	0 0 3	0.04	0 0 5	0.10		
Q	89600	81400	74400	71700	70200	69900	69400		
$c \times 10^4$	0.20	0.30	0 40	0.50	0.60	0.70	0.80	0.90	
Q	66800	58900	40800	32200	25300	21300	7690	7570	
$c \times 10^4$	1.0	1.5	2 0	2 5	3.0	3.5	4 0	4.5	5.5
Q	7390	6050	5140	4690	4430	4250	4220	4180	4180

of experimentation is not known at this time so the curves were drawn to follow the data obtained. The resulting values of Q are plotted in Fig. 2 and the curve so obtained is smoothed at this point as shown.

Interpretation of Results

Like the curve of Keyes and Marshall, the present curve shows a tendency to flatten in the vicinity of 70,000 calories. Instead of ending abruptly at 72,000 calories, however, the data indicate a rapidly increasing differential heat not differing much from 89,600 calories for zero concentration. The final heats of adsorption at large values of c are practically the same as those of Keyes and Marshall. The numerical accord between the earlier work and the present indicates that the general adsorptive characteristics of wood and coconut charcoal are not different, at least as far as the adsorptive heats of oxygen are concerned.

With few exceptions the Q–c curves obtained by other investigators have shown a maximum value of Q at zero concentration. This can be explained in terms of the hypothesis suggested by Langmuir[4] for adsorption and Taylor[5] for contact catalysis, that the surface atoms are of unequal activity. The gas would be expected to adsorb on the more active atoms first, and assuming that the heat of adsorption is an approximate measure of the activity of the surface atoms, a maximum differential heat of adsorption would be obtained at the lower concentrations. In the case of the adsorption of hydrogen on metal catalysts, which forms an exception to the above rule,[6] it must be assumed that here the heat of adsorption is not a measure of the activity of the surface atoms.

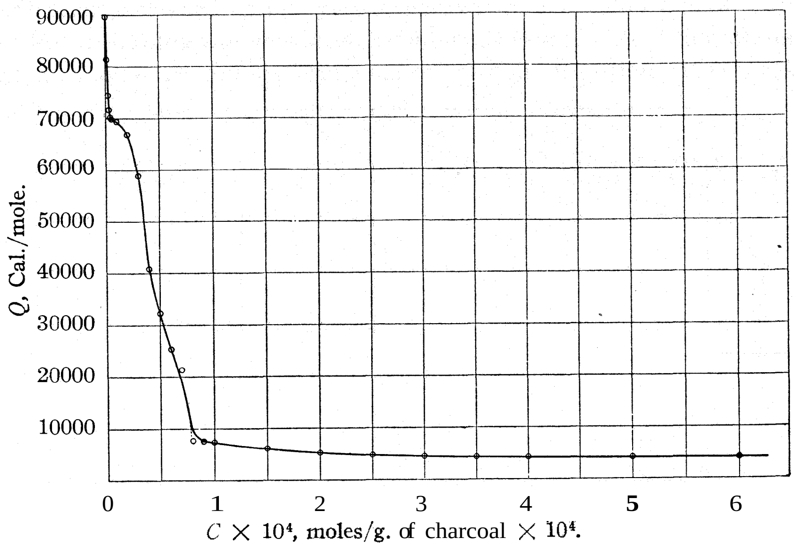

Fig. 2.

If some value c_0 is considered to represent the concentration at which the surface is covered, we can plot $c_0 - c$ against the corresponding values of Q and obtain an integral distribution curve giving values of Δc equal to those from Fig. 2, but with a positive sign. From the slopes of this last curve at various values of Q we obtain $\mathrm{d}(c_0 - c)/\mathrm{d}Q = -\mathrm{d}c/\mathrm{d}Q$. These values of $-\mathrm{d}c/\mathrm{d}Q$ were accordingly obtained from Fig. 2 by measuring graphically at various values of Q the slopes of the curve, and their sign was then changed. These results are given in Table III and plotted in Fig. 3.

This last curve (Fig. 3) is a distribution curve of the type used to describe the distribution of gas velocities. In such curves the area under the

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[4] Langmuir, THIS JOURNAL, 40, 1361 (1918).

[5] Taylor, *Proc. Roy Soc. London,* **108A,** 105 (1925).

[6] (a) Beebe and Taylor, THIS JOURNAL, **46,** 43 (1924); (b) Fryling, *J. Phys. Chem.,* 30, 818 (1926); (c) Kistiakowsky, Plosdorf and Taylor, THIS JOURNAL, 49,2200 (1927).

TABLE III

RESULTS

Q	89600	80000	75000	72000	71000	70000	69800	69600	69400
$-dc/dQ \times 10^9$	0.110	0.132	0.175	0.464	0.594	1.795	12.595	9.443	6.431

Q	69000	68000	66000	60000	50000	40000	30000	20000	10000	8000
$-dc/dQ \times 10^9$	5.224	3.484	1.868	0.899	0.462	0.850	1.370	1.524	0.242	0.000[a]

[a] The choice of this value is explained below under the heading "Thickness of the Adsorbed Layer."

curve between any two energy values represents the fraction of the total number of molecules present having energy values between these limits. In the present case, because the number of molecules required to cover the surface is still a matter for debate, we have preferred to choose our variables

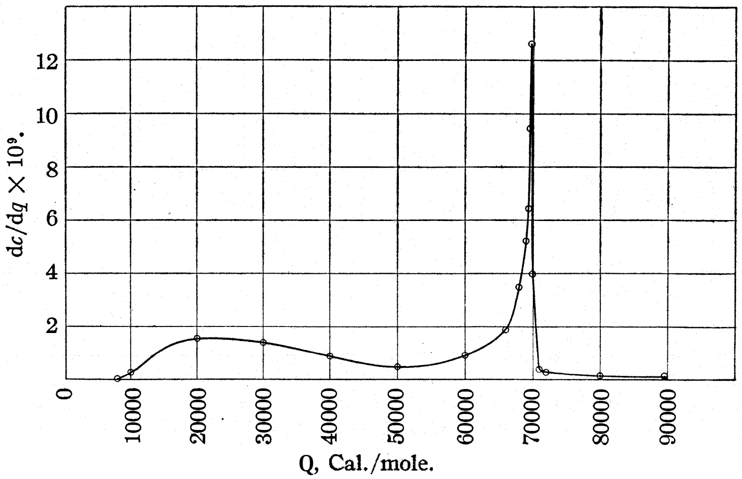

Fig. 3.

to make the area between any two values of Q equal to the number of moles of oxygen per gram of charcoal with heats of adsorption between these limit. That is, $\int_{Q_1}^{Q_2} dc/dQ.\ dQ = \int_{c_1}^{c_2} dc$. As pointed out previously, this change of c between Q_1 and Q_2 can be obtained from Fig. 2. These integral values of c can be regarded as equivalent to Langmuir's elementary spaces per gram of charcoal. It is difficult to discuss the relative activities of individual carbon atoms, as all the surface atoms probably cannot hold the same amount of oxygen. Furthermore, one carbon atom can represent two different heats of adsorption, a high heat for the first addition of oxygen, and a lower heat for a later second addition.

It is evident that the curve, as a whole, does not resemble a probability curve in form. Probability distribution in the present curve would be most likely to exist above 70,000 calories, although the probability function

$y = 2h/\sqrt{\pi} \times e^{-(hx)^2}$ could not be made to fit the curve over this range. The present curve shows a much more uniform distribution in this region than the error curve. It is evident that a slight relative error in the values of q in the extremely low concentration range would alter the shape of the distribution curve (Fig. 3) considerably, so that a large amount of exact experimental data is necessary before a decision can be reached regarding the application of such distribution functions. A knowledge of the distribution of surface activities is very desirable, as it would enable a study of cataiyzed reactions to be made under controlled conditions of surface activity and distribution.

That a similar distribution of the more active centers occurs on some other adsorbents as well is shown by the Q-c curve of Beebe[7] for carbon monoxide on a copper catalyst, and a similar curve for carbon dioxide on charcoal by Magnus and Kälberer,[8] which resemble the present curve in the particular that the curve becomes almost parallel with the Q axis as c approaches zero. Even for the heat of adsorption of hydrogen on nickel, where the initial heat is abnormally low, Fryling[6b] assumes that extrapolation of the final portion of the curve back to small values of c would cause it to approach the Q axis in the same manner.

The flattening of the Q–c curve, similar to that at 70,000 calories for the previous work[1] and the present investigation, is not so common. Polanyi and Welke[9] obtain Q-c curves for sulfur dioxide on charcoal which increase rapidly with decreasing c and show a tendency to flatten at the same molecular concentration ($c = 0.1 \times 10^{-4}$) as the present curve. The resulting maximum in the distribution curve (Fig. 3) at about 70,000 calories possibly represents some definitely recurring state or position of the surface carbon atoms.

Thickness of the Adsorbed Layer.—Keyes and Marshall have found linear relations between the final heats of adsorption at high concentrations and certain constants of the normal molecule which led them to the conclusion that the final heats of adsorption resulted from adsorption on previously adsorbed layers. If, then, we assume for the time being that the entire extent of the Q–c curve represents the formation of multiple layers, the point at which a single primary layer is completed would in general be represented by a zero or a minimum value of $-\mathrm{d}c/\mathrm{d}Q$, provided that extensive overlapping of layers does not occur. There are two points on the Q-c curve which approach this condition, first, the steep part of the curve at $c_a = 0.35 \times 10^{-4}$, and second, the inflection resulting from smoothing of the discontinuity at $c_b = 0.78 \times 10^{-4}$. If the data were followed strictly $-\mathrm{d}c/\mathrm{d}Q$ at c_b would be zero, as can be seen from the

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[7] Beebe, *J. Phys. Chem.*, **30, 1538 (1926).**

[8] **Magnus and Kälberer, Z.** *anorg. Chem.*, **164, 345 (1926).**

[9] **Polanyi and Welke,** *Z. physik. Chem.*, **132,371 (1928).**

position of the points in Fig. 2. For the construction of the distribution curve (Fig. 3) this zero slope at c_b has been used, although in the actual Q-c curve (Fig. 2) we have given $-\mathrm{d}c/\mathrm{d}Q$ a small positive value at this point, as zero slope would not be expected experimentally either at c_a or c_b due to some overlapping of layers.

Three possible explanations occur to us for the peculiar form of the distribution curve (Fig. 3). (1) The range to $c_b = 0.78 \times 10^{-4}$ represents the formation of a monomolecular or monatomic layer. Fig. 3 gives the variation in activity of the elementary spaces on the surface. (2) As c_b is about twice c_a, the point c_a could represent the completion of a primary layer and c_b a second layer. **(3)** Adsorption of oxygen on one elementary space would tend to decrease the activity of an adjacent space. Thus it can be shown that the heat evolved when an atom of oxygen combines with an atom of gaseous carbon to form carbon monoxide is several times as great. as that evolved when an atom of oxygen combines with a molecule of carbon monoxide to form carbon dioxide. This decrease in the activity of adjacent spaces might create a preponderance of elementary spaces having the lower heats of adsorption, and possibly cause a deficiency among the spaces with intermediate heats. Such a state of affairs would produce the minimum found on the curve (Fig. 3) at intermediate Q values, thus showing the characteristics of a second layer.

The only other investigation which shows an inflection at c_b is that of Fryling[6b] for hydrogen on nickel, while a minimum value of $-\mathrm{d}c/\mathrm{d}Q$ corresponding to that at c_a is more common. Consequently c_a most probably represents the limit of the primary layer. This rarity of occurrence does not necessarily mean that the c_b inflection is due to experimental errors. It is evident that an overlapping of layers would obscure both inflections, but that at c_b more readily than that at c_a. This would be particularly true for vapors or easily condensible gases whose initial heats of adsorption are low. The above considerations favor (2) or **(3)** but cannot distinguish between them. The authors consider that more data are necessary before forming a definite hypothesis, and the above statement of possibilities is presented with the hope that it will assist in the production of such data.

It is difficult to utilize the Q-c data below c_b for the construction of a distribution curve of the type represented by Fig. 3, because of the comparatively small variation of Q with c. Considerations of kinetic equilibrium would require the formation of an equipotential surface as the layers increase in thickness, the concentration of adsorbed gas being greatest around the most active centers. Over this region the surface would be of uniform activity, which is in accordance with the small variation in Q actually obtained.

Applicability of the Theory of Monomolecular Layers.—From the point of view of the monomolecular layer theory we must assume that oxygen is adsorbing on elementary spaces of the free carbon surface, even at $c = 5.0 \times 10^{-4}$. Examination of the Q–c curve shows that at least 85% of the total elementary spaces have heats of adsorption below 8000 calories. Investigations covering other adsorbents and adsorbates show similar almost constant final heats. The curve of Keyes and Marshall shows practically the same proportion of elementary spaces below 8000 calories as that quoted for the present results. Outgassing of the charcoal between runs should alter considerably this abnormal distribution of elementary spaces by removing some of the carbon atoms as oxides of carbon. The steep part of the Q–c curve would be affected to a much smaller degree, as the distribution over this range is more in accord with probability. In accordance with this possibility, we have noted during our experiments slight variations about a mean of the shape of the curve in this region. On the other hand, the position of the sharp change in slope at c_b varied so little that the proportion of low activity spaces could be considered to remain practically constant. The sum total of evidence at hand seems to show that the position of this change of slope depends mainly on the specific surface of the charcoal, which in turn is a function of the material from which the charcoal is made.

We might, of course, assume that only the more active carbon atoms can activate the oxygen molecule, causing a kind of surface chemical combination, and that the low final heats are due to combination of oxygen molecules with less active carbon atoms by secondary valence only. This would explain the constancy of the low final values, but the hypothesis is still open to the previous objection that it should be possible to shift considerably the position of the change of slope at c_b by heat treatment. Consequently, comparing the assumptions involved in the two opposing views, we believe that the phenomena herein described receive a more plausible explanation from that form of the multimolecular layer theory suggested by Keyes and Marshall.

Calculation of the Specific Surface.—Calculation of the specific surface of the adsorbent from the amount of gas adsorbed is always uncertain, as some assumption must be made regarding the manner in which the molecule is adsorbed. Assumption of a monatomic layer would give the largest surface, while assumption of orientation normal to the surface would give the smallest. As a mean between the two extremes we will consider the total number of molecules which can be packed in a single-layer on 1 sq. cm. of surface to be 0.77×10^{15}, as computed by Langmuir from the molecular volume of liquid oxygen. Assuming completion of the first layer at $c = 0.35 \times 10^{-4}$, we have $(0.35 \times 10^{-4} \times 6.06 \times 10^{23})/(0.77 \times 10^{15}) = 2.8 \times 10^4$ sq. cm. per gram of charcoal. If, on the other hang, we assume the surface layer to be complete at $c = 0.78 \times 10^{-4}$, the specific surface would be 6.1×10^4 sq. cm. per gram.

Other Investigations.—Ward and Rideal[10] have obtained curves for the heat of adsorption of oxygen on four varieties of charcoal. They did not measure initial values of Q, although the curves shown resemble corresponding parts of the present curves. They object to the multimolecular layer theory of Keyes and Marshall because of the dye adsorption work of Paneth,[11] and because the pressure increases indefinitely with the concentration and does not tend to a limiting value at constant temperature. We feel that much work must still be done before the conclusions of Paneth regarding the specific surface of charcoal can be accepted without question. The mode of variation of p with c can hardly be quoted in support of the monomolecular layer theory, as it can be made to fit either theory by making appropriate assumptions regarding the mechanism of the adsorption. The question of layer thickness is reviewed by Rideal.[12]

Garner and McKie[13] report a heat of adsorption for oxygen on charcoal of 5000 calories per mole at 18° between $c = 0.001 \times 10^{-4}$ and $c = 0.006 \times 10^{-4}$, jumping to 60,000 calories at $c = 0.04 \times 10^{-4}$, and then increasing slowly to 71,000 calories at $c = 0.15 \times 10^{-4}$. The present results show no evidence of this low initial value. We could not, of course, investigate the region between $c = 0.001 \times 10^{-4}$ and 0.006×10^{-4}, but from $c = 0.01 \times 10^{-4}$ to $c = 0.04 \times 10^{-4}$ our values are abnormally high rather than abnormally low, as required by the curve of these authors. Further, between $c = 0.0136 \times 10^{-4}$, our lowest measured concentration, and $c = 0$ the slope of the q–c curve shows a marked tendency to increase as it approaches the origin, which is a real point on the curve. Finally, we note that these authors report only one really low value, no heat values between 5000 calories and 60,000 calories having been measured. Since completion of this paper, McKie[14] has described their experimental method in detail. It would be desirable to repeat the above measurements with thermocouples placed at different points throughout the mass of the charcoal and so arranged that the average temperature of the charcoal could be obtained by integration of the results.

Summary

1. The differential heat of adsorption of oxygen on activated coconut charcoal has been measured as a function of the gas concentration on the charcoal, special attention being paid to these values at low concentrations. The maximum heat of adsorption at zero concentration was found to be 89,600 calories per mole of oxygen.

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[10] Ward and Rideal, *J. Chem. Soc.*, 130, 3117 (1927).

[11] Paneth and Vorwerk, *Z. physik. Chem.*, 101, 445 and 480 (1922); Paneth and Thimann, *Ber.*, 57, 1215 (1924); Paneth and Radu, *ibid.*, 57, 1221 (1924).

[12] Rideal, "Surface Chemistry," Cambridge University Press, pp. 139–145, 150–151.

[13] Garner and McKie, *J. Chem. Soc.*, 130, 2451 (1927).

[14] McKie, *ibid.*, 130, 2870 (1928).

2. Similarity of the resulting curve, of heat of adsorption against gas concentration on the surface, to that obtained in previous investigations emphasizes the specific nature of the adsorption and the constancy of the charcoal surface.

3. A distribution curve is obtained showing the apparent distribution of activities of the elementary spaces on the carbon surface. Several possible explanations are advanced for the shape of this curve.

4. From a comparison of the shapes of the initial portions of various Q–c curves certain regularities are noted and it is concluded that there is a possibility of obtaining a mathematical expression for the distribution of the more active elementary spaces on the surface.

5. The conclusion is reached that the results support best that form of the multimolecular layer theory previously suggested by Keyes and Marshall.

6. The specific surface of the charcoal is estimated to lie between 2.8×10^4 and 6.1×10^4 sq. cm. per gram.

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GERMANATE GELS OF THE ALKALINE EARTHS

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The soluble salts of the alkaline earths cause no precipitation in neutral or acid solution of germanium dioxide but when such solutions are made alkaline with ammonium hydroxide most of the germanium is thrown down as a bulky gelatinous mass. Under such circumstances, however, it is not easy to form homogeneous or firmly set gels owing to the flocculating influence of the ammonium salt simultaneously produced. If calcium hydroxide solution be substituted for the salt of the same base the reaction with aqueous germanic acid takes on a surprisingly different character, for the precipitate then assumes the form of a firm, transparent gel even in highly dilute solutions. The direct formation of calcium, strontium and barium germanates by neutralization of aqueous germanic acid results in the formation of insoluble or difficultly soluble salts under conditions most favorable to colloid formation, as water is the only by-product in the reaction. At the same time this reaction is peculiarly characteristic for germanium, for all of the other semi-metallic dioxides in the fourth periodic group are quite insoluble in water.

It is the purpose of this paper to describe the alkaline earth germanates when prepared in the form of highly dispersed systems with particular attention to the calcium salt, which appears to give permanent gels of extraordinary water content.

Preparation of Reagents

Germanic Oxide.—The pure dioxide was obtained by hydrolysis of the redistilled tetrachloride and subsequent ignition of the product in superheated steam. The nearly pure oxide so obtained was frequently moistened, dried and ignited to 900–950° to effect the complete removal of traces of chlorine and finally fused to a glassy mass at 1100–1150° in a platinum crucible. (This can be carried out in an electric resistance furnace with careful exclusion of any reducing gases, but any direct flame touching the crucible results in quick reduction and destruction of the platinum crucible.) The glassy mass of oxide was dissolved in boiling water, using approximately one liter of water for each 5 g. of oxide. After determination of the GeO_2 content of aliquot portions of this solution the bulk was diluted to definite molarity.

Calcium Hydroxide.—Selected crystals of Iceland Spar were ignited in platinum and the residual lime was dissolved in freshly distilled water. The saturated solution of lime water was siphoned off into paraffin-lined flasks and sufficient carbon dioxide-free water was added to dilute beyond the saturation point at room temperature. The exact content of calcium oxide was determined in aliquot portions gravimetrically as calcium sulfate.

Strontium Hydroxide.—Baker's Analyzed $Sr(OH)_2 \cdot 8H_2O$ was dissolved in redistilled water and preserved in paraffin-lined flasks.

Barium Hydroxide.—Baker's Analyzed $Ba(OH)_2 \cdot 8H_2O$ was dissolved in redistilled water. The nearly saturated solution was siphoned off into paraffin-lined flasks and subsequently diluted to solutions of definite concentration.

Water.—The distilled water of the laboratory was redistilled in fresh portions as required, rejecting first and last fractions, collecting middle fractions in paraffin-lined flasks.

Alcohol.—Alcohol was distilled first from lime and then from shavings of metallic calcium.

Ether and benzene were redistilled and dehydrated over metallic sodium.

Flasks, pipets and burets were calibrated at 22–25°.

Calcium Germanate Gels

Preliminary experiments were made with 0.0279 N calcium hydroxide and solutions of germanic acid of gradually decreasing concentration, as indicated in Table I. It was immediately observed that calcium germanate formed translucent or transparent gels throughout wide ranges of dilution of acid and base but also that homogeneous gels could only be obtained when the reacting base and acid were rapidly and thoroughly mixed. The following procedure gave most satisfactory results: base and acid were separately drawn off from burets into paraffin-lined beakers and simultaneously poured into a third beaker in which gelation took place. If kept free from dust particles the fresh surface of paraffin allows complete transference of the measured volumes in the few seconds between initial mixing and subsequent gelation.

In the first series of experiments calcium hydroxide and germanic acid were mixed in the calculated ratio for the formation of the salt of hypothetical ortho-germanic acid, ($2CaO:GeO_2$), carrying out the gel formation at 25°. At this temperature, if the mixture is quickly made, the combining acid and base stiffens to an opalescent gel in three to five seconds and during the next minute or two the somewhat uneven cloudiness in the gel mass disappears, leaving an almost clear and colorless permanent gel.

A firm gel was obtained by mixing 108.4 cc. of calcium hydroxide solution containing 0.1122 g. of CaO with the same volume of aqueous germanic acid containing 0.1045 g. of GeO_2. These quantities correspond to $2CaO:GeO_2$ (molar weights expressed in mg.). The volume of the gel was then 216.8 cc. and must have contained 0.2167 g. of total anhydrous solids ($CaO + GeO_2$). The gel appeared perfectly dry and was firm enough to allow inversion of the containing beaker (250 cc.) without loss. The extraordinary dispersion of the calcium salt is evident, for the gel contained 99.90% of water bound or trapped by as little as 0.10% of anhydrous constituents. Otherwise expressed, 0.0184 M CaO reacts with 0.00922 M GeO_2 with the formation of a solid gel, although the gel contains no more than 1/1000 of its weight of anhydrous oxides

Properties of Calcium Germanate Gel.—Samples of the solid gel prepared as above were preserved in a large desiccator over dilute sodium hydroxide to prevent drying and contamination by carbon dioxide and after standing for nearly a year showed no sign of syneresis. Exposed to air some drying takes place with slow formation of an opaque white surface as carbon dioxide is taken up. Other samples were broken down by stirring rapidly with a spatula or glass rod and when the mechanically broken gel was thrown on a Büchner funnel it was found that almost all of the trapped liquid could be removed by suction alone, leaving a small residue of the calcium salt on the filter. This residue closely resembles macerated filter paper pulp and after drying at room temperature or at 100° can be almost completely removed from the filter in a single piece. It is almost infusible, but on strong ignition shrinks considerably with the loss of 14–20% of water held by the air-dried salt. The hydrogel is dissolved by 0.2 M calcium chloride and by ammonium chloride but is nearly insoluble in the fixed alkali chlorides. Before and after ignition calcium germanate is insoluble in water but is readily soluble in dilute mineral acids. 0.2 N hydrochloric acid slowly dissolves the ignited salt and as germanic acid has no effect on methyl orange the CaO content of the salt can be determined by titrating back the excess of acid with standard sodium carbonate. This method gives a rapid check on the composition of the salt.

Microscopically examined the gel itself appears to be amorphous but under highest power (1700–1800 diameters) some indication of crystalline structure appears indistinctly, especially in the ignited salt.

Effect of Temperature.—As calcium germanate gel is so easily broken down by mechanical means, such as violent agitation or suction filtration, it was thought that elevation of temperature would bring about a rapid syneresis, but unexpectedly the gel when once produced resisted temperature changes up to near the boiling point of water. A number of tubes containing the gel were tightly stoppered and immersed in thermostatic baths. The gels all remained unchanged up to 75°. At 100° numerous entrapped bubbles in the gel greatly increased in size, causing separation of a small amount of liquid. Gels which had been heated to 90–95° showed practically no change.

An attempt was made to reproduce the gel by combining hot solutions of both acid and base but under such conditions no gelation occurred. At 60–70° calcium hydroxide and germanic acid gave only well flocculated white precipitates of small volume which settled rapidly and could not be subsequently deflocculated. The solutions of acid and base were then chilled to 0° before mixing and on combining these it was found that gelation did not take place in the cold. The mixtures remained liquid and perfectly clear for some time but on allowing the temperature to rise slowly to 25° almost water-clear solid gels resulted. From these experiments it would appear that the velocity of gelation is greatly cut down by small reduction in temperature and that any appreciable rise above room temperature results in too rapid a precipitation of the salt for any colloidal structure to build up. The latter condition is connected with imperfect mixing of the acid and base, for it was impossible to obtain any homogeneous gel unless an appreciable interval of time was allowed for a fairly good mixture of the two reacting liquids. With the warm acid and base precipitation was instantaneous. The best temperature for gel formation lies between **15** and **25".**

Several gels prepared at 25° were chilled to −17°. The expanding ice crystals increased the volume of the gel, which assumed a rounded or dome-shaped surface. After complete freezing the hard mass was allowed to melt slowly. All signs of gelation had disappeared, leaving a comparatively small precipitate from which the separated liquid could be poured off.

Substitution of the Water of the Hydrogel by Other Liquids

Ethyl Alcohol.—Hydrogels containing **99.90%** of water were prepared under conditions favoring firmest set. Conditions are shown in Table III, Expts. 1 and **2,** but employing larger volumes. Gel masses of **250** cc. each were used. The hydrogel was immersed in a large excess of **95%** alcohol. The gel became much firmer to the touch when so treated and could then be more easily cut up into smaller blocks or cubes. Cubes of about **8** cc. each were selected and again washed with fresh alcohol until most of the water had been removed. Complete extraction was carried out in the Soxhlet apparatus using absolute alcohol. The return alcohol was discarded a number of times, using fresh, dry alcohol and continuing the extraction until the return liquid gave approximately the same density over twenty-four-hour periods. A portion of the gel was selected and the trapped alcohol removed on a dry suction filter. The filtrate protected from moisture gave a density of **0.7949.** The original alcohol was d_{16}^{16}, **0.7943,** which value corresponds to **99.8** to **99.9%** alcohol by volume.

As alcohol substituted the water of the hydrogel there was a corresponding fall in specific gravity of the immersed gel and near the end of the extraction the cubes of gel became light enough to remain suspended in the surrounding liquid for a few moments and at the same time the gel mass, which was easily visible beneath the alcohol as long as water was present, became scarcely visible when nearly all of the water was removed. The changes in both specific gravity and refractive index conveniently show the end-point in the extraction process, making a larger number of density determinations unnecessary.

Methyl Alcohol.—The hydrogel was extracted with pure dry methyl alcohol in the same manner as that described above. In this case the gel volume decreased somewhat more than **50%.** The methyl alcohol gel although smaller in volume was softer and less easy to handle than the ethyl alcohol gel. It could, however, be cut into thin slices with a sharp knife without loss of any liquid and was permanent when kept in a well-stoppered flask.

Ethyl Ether.—Half of the alcohol gel prepared as above was extracted for a number of days with dry ether (distilled over sodium), frequently changing the extracting liquid for fresh ether. As in the case of the ethyl alcohol gel formation there was little change in volume of the gel mass and at the end of several days the cubes of ether gel became specifically light enough to remain suspended for some time in the surrounding ether. Extraction with fresh dry ether was continued until the density of the return ether reached the value for the pure extracting liquid (determined by hydrometer). Some of the cubes of gel were removed from the ether and were found to be much firmer to the touch than either the alcohol or water gel from which they had been prepared. Exposed to dry air the ether gel rapidly diminished in volume to a very small irregular fragment which crumbled to a dry powder between the fingers.

Action of Benzene on the Ether Gel.—A part of the ether gel was treated with pure benzene (redistilled over sodium). It immediately contracted to about 40–50% of the original volume, at first becoming milky white and opaque. The opacity was probably due to the formation of some emulsion of benzene and ether, as these two liquids are not miscible in all proportions After long standing the contracting gel again became transparent, especially on the outer portions of the immersed cubes, but complete extraction of the ether was not possible in several weeks' contact with fresh excess of benzene.

All of the above gels have been preserved in tightly-stoppered vessels and appear to be quite permanent, both in the dry state and when immersed in excess of the same liquids trapped by the gel structure. They are all capable of yielding most of their trapped liquid by strong pressure or suction filtering, especially after the gel has been mechanically broken down by violent stirring. Suction filtering yields a residue of the dry or nearly dry salt which appears absurdly small when compared to the original volume of gel. A whole liter of the hydrogel, for example, can be transferred completely to a 9-cm. filter if a platinum cone and suction be applied. The residue on drying at room temperature or at 100° can then be taken out of the filter in a single piece, leaving almost nothing adhering to the filter paper.

While any conjecture as to the actual nature of the highly dispersed calcium germanate in the above gels would be purely speculative, it seems clear that such gels are entirely structural in character, that is to say, practically all of the liquid present appears to be simply trapped by an enormous number of minute filaments of the dispersed calcium salt. At present it is impossible to say whether these are crystalline or amorphous, for the high power microscope at 1700 diameters fails to show more than a faint suspicion of crystalline structure. Further information in this direction may be obtained by x-ray spectral examination of the gel or its dried residue and an effort to obtain such evidence is being made.

Composition of Calcium Germanate.—108.4 cc. of calcium hydroxide containing 0 1122 g. of CaO treated with the same volume of germanic acid containing 0.1045 g. of GeO_2 gave a firm gel of 216.8 cc. After preserving this gel for some hours in a desiccator over dilute caustic alkali, it was broken up by stirring and the whole was transferred to a suction filter. The small mass left on the filter was washed with very little cold water. The residue and filtrate were separately analyzed.

The Residue.—The residue dried at 100° was detached from the filter almost in one piece, leaving scarcely anything on the paper; the latter was separately ashed in a weighed crucible before adding the main bulk of salt. Ignition at bright red heat, weighing before and after, showed that. the dried mass had retained about 13.9% of water at 100°. The ignited salt was dissolved in 6 N hydrochloric acid and all of the germanium removed by saturation with hydrogen sulfide under pressure. The sulfide was filtered off and converted to dioxide in the usual way, weighing as GeO_2. The filtrate containing all of the calcium and much acid was evaporated nearly to dryness and the residual calcium salt was converted to sulfate by continuing the evaporation with excess sulfuric acid, weighing the residual ignited $CaSO_4$. Results of this analysis were 36.43% of CaO and 63.40% of GeO_2 for composition of the ignited salt.

The Filtrate from the Mechanically Broken Gel.—The combined filtrate and wash water was made 6 N with hydrochloric acid and saturated with hydrogen sulfide. Only a very small precipitate of GeS_2 appeared, requiring three or four hours to form. Converted to dioxide this amounted to only 0.0003 g. The filtrate from this small amount of germanic sulfide was examined for calcium by converting the residue obtained by evaporation to calcium sulfate as before. Results showed that the suction filtrate from the original gel was practically pure lime water and that the precipitation of germanium had been about quantitative.

It is also evident that the calcium salt of hypothetical orthogermanic acid cannot be formed by uniting the base and acid in the ratio calculated for this salt, and that the solid produced in the dispersed condition approaches the theoretical composition of calcium metagermanate, $CaGeO_3$ (theoretical values are $CaO = 34.93$, $GeO_2 = 65.07$), about half of the lime water originally added remaining in the free state. An attempt was now made to produce the metagermanate in purer form by combining the base and acid in the calculated ratio for this salt. In this series of gels (some of which are shown in Table II), the expected metagermanate did appear in purer form but a very noticeable change took place in the gelation dilution limit when compared with the gels made in the presence of excess calcium hydroxide. In addition, the second series of gels differed greatly from the first in their lack of clarity, for all of these were milky white or nearly opaque.

Gelation Dilution Limit for Calcium Germanate Gels.—Tables I, II, III and IV show the influence of varying ratios of base and acid upon the gelation dilution limit of calcium germanate gel, the gelation dilution limit being arbitrarily defined as the maximum dilution at which the dispersed salt sets firmly enough to permit the inversion of the container without loss of its contents and without separation of any visible untrapped liquid over a period of several days, gelation being carried out at 22–25° in all experiments.

TABLE I

GELS FORMED BY MIXING CALCIUM HYDROXIDE AND GERMANIC ACID IN THE CALCULATED RATIO FOR THE HYPOTHETICAL ORTHOGERMANATE, $2CaO:GeO_2$

	$Ca(OH)_2$, cc.	CaO, g.	GeO_2, cc.	GeO_2, g.	Gel. vol., cc.	H_2O in gel, %	Remarks
1	30	0.02345	8.85	0.02177	38.8	99.884	Firm gel, sl. cloudy, permanent
2	30	.02345	11.8	.02177	41.8	99.892	Same as 1
3	30	.02345	14.75	.02177	44.7	99.899	Firm gel, clearer than 1 and 2
4	30	.02345	14.75	.02177	44.7	99.899	Same as 3
5	30	.02345	17.7	.02177	47.7	99.905	Firm gel, nearly cl., no water sep.
6	30	.02345	23.6	.02177	53.6	99.915	Stronger gel than 7
7	30	.02345	29.5	.02177	59.5	99.924	Very clear, fairly firm set
8	15	.00782	15.0	.00729	30.0	99.950	Not firm, falls from inv. cont.
9	15	.01172	17.7	.01088	32.7	99.931	Poor gel, some water sep.
10	15	.01172	23.6	.01088	38.6	99.941	Not very firm set gel
11	15	.01172	24.1	.01088	39.1	99.942	About same as 10
12	30	.02345	29.5	.02177	59.5	99.924	Fair gel, not very firm set
13	108.3	.11218	108.3	.10450	216.6	99.900	Quite firm, clear gel, remains in inverted container

The results shown in Table I indicate that the gelation dilution limit for mixtures of calcium hydroxide and germanic acid lies between fairly narrow limits of water content, for those gels containing more than 99.92% of water do not set firmly, while those containing less than 99.88% of water are cloudy and give evidence of too rapid a precipitation of the calcium salt to allow the highest dispersion. All gels in this table are prepared by combining acid and base in the $2CaO:GeO_2$ ratio and inspection of the other tables (II, III and IV) will show that varying the proportions of acid and base results in noticeable change in dilution limit.

The best working conditions for the formation of good gels for this ratio of acid and base appear to be found at dilutions corresponding to 99.90% of gel water, as shown in Table I, Expt. 13.

Table II

Calcium Germanate Gels Produced by Combining Acid and Base in Calculated Ratio to Form the Calcium Salt of Hypothetical Metagermanic Acid, $CaGeO_3$, Showing Gelation Dilution Limit for Gels So Prepared

	$Ca(OH)_2$ soln, cc	CaO, 6	GeO_2 soln, cc.	GeO_2, g.	Vol of gel	H_2O in gel, %	Remarks
1	30	0.02345	29.5	0.04354	59.5	99.887	Cloudy white, not very firm gel
2	30	.02345	29.5	.04354	59.5	99.887	Cloudy wh., few water drops sep.
3	25	.01954	14.85	.03653	39.85	99.859	Cloudy white, fairly solid
4	25	.01954	18.8	.03653	43.8	99.872	Poor gel, water sep.
5	25	.01954	29.7	.03653	54.7	99.897	Very poor gel, white, not firm
6	30	.01172	8.85	.02177	38.85	99.914	No gel at all, ppt. sep.
7	25	.01954	13.9	.03653	38.9	99.856	Fairly firm, white gel
8	25	.01954	9.9	.03653	34.9	99.839	Like 7 but little firmer
9	80.3	.05609	80.3	.10450	160.6	99.900	Very poor gel with sep. water
10	160.6	.11218	160.6	.20900	321.2	99.900	About same as 9

From the ten experiments shown in Table II it will be seen that the combination of calcium hydroxide and germanic acid in the $CaO:GeO_2$ or 1:1 ratio also brings about gelation at relatively high dilution but the gelation dilution limit in this case is reached when the water content becomes 99.83 to 99.85%; the gels in Table I made in the $2CaO:GeO_2$ ratio of base to acid reached limiting dilution at about 99.90% of water (see No. 7, Table I, and compare with No. 7, Table II, as representing dilution limit in these two systems). In these gels it is seen that No. 7, Table I, offers a gel containing 0.04322 g. of total anhydrous solids per 59.5 cc. of gel and No. 7, Table II, a gel containing 0.05607 g. of anhydrous constituents per 38.9 cc. of gel volume. Calculating these to the same volume of gel in each case, the limiting values for anhydrous oxides in the two become 0.07596 g. per 100 cc. of gel of the ortho, ratio $2CaO:GeO_2$ for Table I, and 0.15138 g. of anhydrous oxides per 100 cc. of gel of the meta, ratio $CaO:GeO_2$ for Table II. These values show the real difference in gelation dilution limit in the two series of gels more clearly than simple expression of their respective water percentages and point out that the content of anhydrous oxides per cc. of gel made as in Table I is only about half that required for a gel of similar consistency made as in Table II.

In addition to variation in dilution limit in the two series of gels it is to be noted that those in Table II are all white and almost opaque and lack the almost water-clear, homogeneous character of those formed under the conditions in Table I.

The previously described analyses of the gels of Table I showed that the composition of the dispersed solid, mechanically freed from trapped water and ignited, approached the theoretical composition of calcium metagermanate and that the trapped water was almost pure lime water which had remained uncombined with germanic acid. These facts together with the poorer gelation obtained under the conditions in Table II indicate that a certain excess of free or uncombined base greatly favors gelation, although the dispersed calcium salt approaches the composition of calcium metagermanate in both cases.

A large quantity of gel was prepared under the conditions shown in Table II, Expt. 7, and the milky white mass was broken up mechanically and sucked as dry as possible on a Büchner funnel; residue and filtrate with wash water now were separately analyzed in the way already described. The residue on the filter after ignition contained 64.12% of GeO_2 and 35.80% of CaO (the theoretical values for $CaGeO_3$ are 65.07 and 34.93). The filtrate drawn from the original gel mass contained germanium which had evidently escaped precipitation in the solid structure of the gel. Complete analysis of this filtrate showed that the total solids present amounted to only about 10% of the total solids present in the original gel and that of this dissolved portion 34.44% was CaO and 65.66% was GeO_2. Evidently germanium is not completely precipitated by mixing calcium hydroxide and germanic acid in the $CaO:GeO_2$ ratio, as in Table II, although $CaGeO_3$ is produced in both this or the former ratio $2CaO:GeO_2$ of Table I. On the other hand, analyses of the gels of Table I showed that the germanium was completely precipitated by the excess lime water and was to be found in the solid gel structure and not in the trapped water.

The fact that the dispersed calcium salt is the same in composition ($CaGeO_3$), whether the base is added in considerable excess as in Table I or in the calculated amount to produce this salt as in Table II, naturally leads to the belief that a certain excess of base is required to favor the formation of homogeneous gels at high dilution as well as to quantitatively precipitate the germanium in the solid or filterable structure of the gel. In the next series of gels, described in Table III, the base and acid were added in a ratio intermediate between those of the former two tables, that is, the $4CaO:3GeO_2$ ratio. Examination of this table will show that by so uniting the base and acid the gelation dilution limit was still further advanced and firm gels of the highest dilution could be so obtained. It was at first thought that the better gelation under these circumstances was connected with the formation of the calcium salt of a hypothetical trigermanic acid but analyses of these gels, seen under Table III, show that again the salt produced was nearly pure calcium metagermanate and that the union of base and acid in the above ratio simply furnished a still more favorable hydroxyl-ion concentration for best gelation.

TABLE III

CALCIUM GERMANATE GELS FORMED BY UNITING BASE AND ACID IN THE CALCULATED RATIO, $4CaO:3GeO_2$, SHOWING GELATION DILUTION LIMIT FOR THIS RATIO

	$Ca(OH)_2$ soln., cc.	CaO, g.	GeOz soln., cc.	GeO_2, g.	Gel vol., cc.	Gel comp.,		Remarks
						% H_2O	CaO + GeO_2	
1	**89.64**	0.07478	**89.64**	0 10450	**179.28**	99.90	0.10	**Firm clear gel in 10 sec.**
2	**26.9**	.02243	**26.9**	.03135	**53.8**	**99.90**	**.10**	**Same as 1**
3	**40.7**	.02243	**40.7**	.03135	**81.4**	**99.935**	.065	**Firm clear gel in 2 min.**
4	**45.7**	**,02243**	**45.7**	.03135	**91.4**	**99.942**	.058	**Gel in 3 min., not firm set, falls from beaker**
5	53.5	.02243	53.5	.03135	107.0	**99.947**	.053	**Bulky mass, will not set**
6	78.68	.08971	85.28	.1254	163.96	**99.869**	.131	**Firm, clear gel in 2–3 sec., remains in inv. vessel on shaking**

Results indicated in Table III show that the mixture of calcium hydroxide and germanic acid in the $4CaO:3GeO_2$ ratio gives the conditions which favor greatest dispersion of the precipitated calcium salt. Experiments 3 and 4 mark the gelation dilution limit between 99.93 and 99.94% of water. Gel No. 3 is particularly interesting because, as far as the writers can ascertain, no gel of comparable water content has thus far been reported in the literature of colloids either in the organic or inorganic field; the total anhydrous oxides present in this dispersed salt is less than a fifth of the anhydrous components found in previously known colloidal dispersions. A liter of this gel (No. 3) contains 0.27579 g. of CaO and 0.38510 g. of GeO_2 or *a* total solid content of 0.66089 g. It will keep indefinitely (over a year), without any syneresis and if kept in a tightly-stoppered vessel will resist any change up to near the boiling point of water. Any quantity of this gel can be prepared by quickly combining equal volumes of 0.009837 *M* CaO and 0.00737 *M* GeO_2.

The $4CaO:3GeO_2$ gel prepared as in Expt. 6, Table III, and containing 0.08971 g. of CaO and 0.1254 g. of GeO_2 in the gel volume of 163.96 cc. was broken up by actively stirring and the whole was filtered by suction, using a platinum cone and filter paper. The small residue on the filter after washing with a small amount of cold water was ignited and analyzed by the method before described. The ignited salt contained 36.42% of CaO and 63.48% of GeO_2. The filtrate plus wash water contained less than 0.001 g. of GeO_2 and 0.0087 g. of CaO, nearly all of which was present as free base. Again it is seen that the insoluble structure of the gel is essentially calcium metagermanate. The GeO_2 found in the ignited salt is low by about 2% when compared with the theoretical value for GeO_2 in this salt and the value for calcium is correspondingly high. It is believed that this discrepancy can be explained in two ways—first, the complete washing of the colloidal residue is difficult on account of adsorbed calcium hydroxide and, second, the alkaline filtrate or trapped gel water quickly takes up carbon dioxide if exposed to the air during filtration—both of these effects result in apparent rise in CaO content of the salt and corresponding low values for GeO_2 found in the filtered residue.

TABLE IV

Calcium Germanate Gels Obtained by Combining Calcium Hydroxide and Germanic Acid in the Ratio $3CaO:2GeO_2$, Showing Gelation Dilution Limit

	$Ca(OH)_2$ soln, cc	CaO, g	GeO_2 soln, cc	GeO_2, g	Gel vol., cc.	Gel comp., % H_2O	% solids ($CaO + GeO_2$)	Remarks
1	94.32	0.08414	94.32	0.10450	188.63	99.900	0.100	Firm clear gel, sets in 1 min.
2	25.0	.02140	33.5	.02670	58.5	99.918	.082	Not firm gel, some liq. sep
3	25.0	.02140	32.2	.02670	57.2	99.916	.084	Fairly firm, some water sep.
4	25.0	.01290	25.0	.01610	50.0	99.942	.058	No geln., ppt. settles to bottom
5	22.5	.01290	22.5	.01610	45.0	99.936	.064	Only partial geln., much liq. sep.
6	26.0	.02140	26.0	.02670	52.0	99.908	.092	Fair gel, sets in 2-min. diln. limit in this series

Table IV shows that the gelation dilution limit for mixtures of calcium hydroxide and germanic acid in the $3CaO:2GeO_2$ ratio is reached at a water content of 99.908 or total solid content of 0.092% but brings out the fact that no gelation will take place at the maximum dilution for gels of the $4CaO:3GeO_2$ ratio in Table III (compare Expts. 3 and 4, Table III, with Expt. 4, Table IV).

Analysis of the gel obtained in Table IV, Expt. 6, showed that the filtrate obtained by mechanical destruction of the gel and suction filtration was essentially free lime water but 0.0023 g. of GeO_2 had escaped precipitation and was also present in the alkaline filtrate. The insoluble portion, which had previously built up the gel structure, on ignition contained 65.40% of GeO_2 and 39.52% of CaO. These results are close to the calculated values for $CaGeO_3$.

Combining all of the results obtained from Tables I to IV, inclusive, it can be safely concluded that more or less pure calcium metagermanate is precipitated by any excess of calcium hydroxide on germanic acid and that this salt alone is responsible for the gelation phenomena observed. Also solid gels are obtained at maximum dilution when acid and base are combined in the $4CaO:3GeO_2$ ratio, Table III, Expt. 3, giving conditions for the most highly dispersed salt obtainable in any known circumstances. This gel contains 99.935% of water and 0.065% of total anhydrous constituents.

Strontium Germanate

Solutions of strontium hydroxide and germanic acid do not form homogeneous gels at dilutions comparable to those used in the formation of the colloidal calcium salt. Strontium germanate gels can be formed, however, if the solutions of acid and base are made up to concentrations of four or five times the molarity of those used under the calcium gels. For this purpose 0.047 M SrO (4.9040 g. of SrO per liter) and 0.049 *M* GeO_2 (5.1450 g. of GeO_2 per liter) were used for preliminary experiments.

Strontium germanate gels were prepared under the same general conditions as those described under the calcium salt, combining acid and base in ratios analogous to those already given. All of the strontium gels were opaque or almost opaque in distinction to the transparent or nearly water-clear calcium gels. The strontium gels set much more slowly and under no conditions could be obtained free from enclosed flocculated masses or aggregates of precipitated salt which interfered with the direct passage of light through the solid gel.

Analyses of the strontium gels were made in exactly the same manner as under the calcium gels. The results of these analyses showed that an excess of strontia ($2SrO:GeO_2$) precipitates nearly all of the germanium which appears in the insoluble and filterable solid structure of the gel, the filtrate obtained by suction and violent agitation of the gel being nearly pure strontium hydroxide. On the other hand, in the formation of the strontium germanate under circumstances where the acid and base were combined in any other ratio approaching the 1:1 molecular ratio, there always resulted an incomplete precipitation of the germanium, much of which then passed into the entrapped gel water. The gel residues obtained by suction were all ignited and analyzed and as under the calcium salt it was found that the salt of metagermanic acid in a greater or less degree of purity was always produced, no matter what excess of strontia had been added to the solution of germanic oxide. In mixtures containing the greatest excess of base ($2SrO:GeO_2$), the residual salt after suction filtration contained 56.10% of GeO_2 and 44.01% of SrO. Calculated values for $SrGeO_3$ were 50.21% of GeO_2 and 49.79% of SrO. The gels formed by combining the strontia and germanic acid in the $SrO:GeO_2$ ratio gave 50.66% of GeO_2 and 49.30% of SrO for the composition of the similarly obtained residue.

The gelation dilution limit for strontium germanate is shown in Table V, but as this salt does not show the unusual dispersion of the corresponding calcium compound, only a few typical experiments are shown, combining in one table the limiting dilutions for various mixtures of base and acid.

From the results shown in Table V it may be concluded that strontium germanate gels cannot be obtained with more than 99.75% of water. The gelation dilution limit for these gels is reached at about 0.25% total

TABLE V

STRONTIUM GERMANATE GELS

Showing gelation dilution limit for mixtures of base and acid in several molecular ratios: $2SrO:GeO_2$; $SrO:GeO_2$; $4SrO:3GeO_2$

	$Sr(OH)_2$ soln., cc.	SrO, g.	GeO_2 soln, cc.	GeO_2, g.	Vol. of gel, cc.	Comp. of gel, % H_2O	Comp. of gel, % solids (GeO_2 + SrO)	Remarks
	Gels 1 to 4 made by uniting base and acid in the $2SrO:GeO_2$ ratio							
1	42.1	0.2060	20.3	0.1045	62.4	99.5	0.50	Firm milky white opaque gel
2	31.2	.1030	31.2	.0523	62.4	99.75	.25	Imp. geln. sets in half min., a little water sep.
3	38.8	.0515	38.8	.0261	77.6	99.90	.10	No gel forms, ppt. sep. in 10–15 min.
4	50.4	.2060	50.4	.1045	100.8	99.70	.30	Fairly firm gel, milky translucent
	Gels 5, 6 and 7 made by mixing base and acid in the $SrO:GeO_2$ ratio							
5	21.05	.1030	20.3	.1045	41.35	99.51	.49	Firm opaque white, sets in 1 min.
6	41.35	.1030	41.35	.1045	82.7	99.75	.25	Fairly firm gel, sets in 1 min.
7	58.15	.1030	58.15	.1045	116.3	99.83	.17	Very poor gel, sets to semi-solid in 1 min.
	Gels 8 and 9 made by mixing base and acid in the $4SrO:3GeO_2$ ratio							
8	72.7	.2072	72.7	.1568	145.4	99.75	.25	Firm opaque gel, sets in 1 min.
9	50.0	.1036	50.0	.0784	100.0	99.82	.18	Poor geln. with sep. of some liq.

solid content ($SrO + GeO_2$), which is about twice the amount of anhydrous material present in solid gels of the calcium compound. The solid structure of these gels is made up essentially of strontium metagermanate, $SrGeO_3$, although the pure salt is rather difficult to isolate from excess of adsorbed strontia. There appears to be no indication of the formation of any other germanate of strontium no matter what excess of strontia is mixed with germanic acid.

Barium Germanate

Unlike the corresponding calcium and strontium salts, barium germanate is appreciably soluble in water, so that mixtures of baryta and germanic acid at dilutions comparable to those used under the calcium and strontium gels gave nothing more than clear solutions in which only partial precipitation of the barium salt occurred on long standing.

Experiments were carried out with more concentrated solutions, using baryta containing **0.00927** g. of BaO per cc. and germanic acid containing **0.00372** g. of GeO_2 per cc.

Sixty-six and two-tenths cc. of barium hydroxide containing **0.61348** g. and **56.2** cc. of germanic acid containing **0.2090** g. of GeO_2 were combined. **A** fine crystalline precipitate formed almost immediately and on standing for some time larger crystals were deposited which collected in shining aggregates on the sides and bottom of the beaker. The crystalline mass was filtered off on a suction filter, washed with a small amount of cold water, dried, ignited and weighed. This amounted to 0.2947 g., representing only 35.8% of the total oxides in the original mixture. Analysis of the ignited salt gave 58.68% of BaO and 41.30% of GeO_2 (theoretical values for $BaGeO_3$ are 59.41 and 40.58). The alkaline filtrate from the original precipitation of the crystalline barium salt contained 0.089 g. of GeO_2 which had escaped precipitation, although the base had been added in double the amount required to form the metagermanate. It will be noted that a corresponding excess of either calcium or strontium hydroxide would have quantitatively precipitated the germanium.

A portion of crystalline barium metagermanate was prepared by combining barium hydroxide and germanic acid in the calculated amounts to form pure $BaGeO_3$, warming the solution of acid and base before mixing the two. In this case the solution remained clear for a few moments and on standing for some time partial precipitation took place as before but the crystals were much larger. Analysis of this distinctly crystalline mass gave 59.64% of BaO and 40.46% of GeO_2, values which are fairly close to the calculated composition of $BaGeO_3$. Under the microscope the crystals appeared to be octahedral in habit and further examination under the polarizing prism showed them to be isotropic. The crystals are very fragile and possibly metastable. The isometric habit of barium germanate is in agreement with the crystalline form of the naturally occurring metatitanate perovskite ($CaTiO_3$) of analogous chemical composition.

Solubility of Barium Germanate.—An excess of finely-powdered crystals of the barium salt prepared as above was shaken with water for a number of days. Using a thermostatic bath at 25°, 100 g. of the solution saturated at 25° contained 0.07536 g. of $BaGeO_3$.

Summary and Conclusion

1. The neutralization of dilute germanic acid by calcium hydroxide produces a colloidal calcium germanate of unusually high dispersion. Firmly set gels are obtained in which the total anhydrous constituents may constitute as little as 0.065% of the gel mass. Gelation at maximum dilution occurs when acid and base are combined in the $4CaO:3GeO_2$ ratio.

2. Calcium germanate hydrogels ranging from 99.90 to 99.94% of water content are permanent dispersoids if protected from dry air and carbon dioxide. Gels may be kept at least a year without syneresis.

3. The water present in dispersed calcium germanate appears to be simply trapped water, nearly all of which can be removed by pressure or suction filtration. The solid structure or filterable mass is pure or nearly

pure calcium metagermanate. All of the germanium is present in the insoluble or filterable structure if the proportion of calcium hydroxide reaches or exceeds the amount present in the molecular ratio $2CaO:GeO_2$.

4. The water of the hydrogel may be replaced by a number of other liquids such as methyl and ethyl alcohol or acetone and these non-aqueous liquids may in turn be replaced by ethyl ether or benzene, yielding a series of non-aqueous dispersoids which are permanent if protected from evaporation.

5. Excess of lime water gives a very delicate and characteristic test for germanic oxide. A small fraction of a milligram of GeO_2 in 20 cc. of water may be recognized on account of the extraordinarily bulky nature of the hydrogel.

6. Strontium germanate yields a dispersoid similar to the calcium salt but gels are not obtained at dilutions comparable to those used in the preparation of the calcium salt.

7. Barium germanate is distinctly different from the calcium and strontium salts. This salt is very distinctly crystalline and appreciably soluble in water. Crystalline $BaGeO_3$ is formed in shining aggregates, probably octahedral. Under the polarizing prism it is shown to be isotropic.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE UNIVERSITÉ LIBRE DE BRUXELLES, LABORATOIRE DE CHIMIE PHYSIQUE]

NOTE ON THE VACUUM CONTRACTION OF DENSITY BULBS[1]

BY MARCEL BECKERS[2]

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Having undertaken the systematic study from a physicochemical point of view of the easily liquefied saturated hydrocarbons, we have been led to assemble at the start a considerable body of experimental material, in order to free ourselves from anxiety over apparatus problems during the measurements.

We had already calibrated a series of gas density bulbs for our measurements of the weight of a liter of *n*-butane,[3] but as regards contraction on evacuation, the values obtained differed in general by 25% from those calculated by the formula of E. Moles and R. Miravalles.[4]

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[3] Beckers, *Bull. soc chim. Belg.*, **36**, 559 (1927).

[4] Moles and Miravalles, *J. chim. phys.*, **21**, 1 (1924).

We have thought it worth while to reopen the question with new measurements. They have been carried out on bulbs numbered **3** to 10, previously calibrated, and on nine new ones, numbered 11 to 20. All the bulbs, whose capacity varied from 600 to 2000 cc., were constructed of Thuringian glass; although we do not know the age of this glass, only bulbs Nos. 6 and 7 devitrified in the flame, and we have not used them further in our work.

The uncertainty of the results obtained by the method of Travers being generally accepted, we have attempted to check them by a method different in principle, namely, the hydrostatic method. Six bulbs (Nos. 6, 15, 16 and 17; 12 and 13) have been measured in both ways. Due to the good agreement obtained, the other bulbs were studied by Travers' method alone.

To attain the desired accuracy, we have had continuously to overcome a number of experimental difficulties. The different investigators who have carried out measurements of this kind have also mentioned meeting obstacles, but unfortunately they have been reticent of details as to their mode of operation. Therefore, we think it worth while to describe our technique in detail, especially as such measurements are slow to make, and their accuracy depends on small factors.

Hydrostatic Method.—The technique adopted differs from that of Moles and Miravalles[4] as follows. The bulb, immersed in a water-bath, is weighed successively evacuated and filled with air. To effect this, the bulb was ballasted by a mass of iron, nickel plated and polished, whose weight was slightly greater than the buoyant force. The iron sinker was suspended by a sort of net made of three pliable brass wires, symmetrically placed in three meridians of the glass sphere, and joined together at the base where the weight was attached by a hook. The upper ends were fastened to another wire forming a concentric loop about one centimeter from the neck of the bulb. In this way, the weight is practically evenly distributed about the neck of the bulb; this region is particularly rigid, and one may assume that no sensible change is made in the amount of contraction by this method of procedure.

The calculation of the results requires knowledge of the weight of air included in the bulb. This quantity is determined by filling the bulb with dry air, freed from carbon dioxide by appropriate washing,[5] and by the knowledge of the interior volume. The pressure of the gas and the temperature of the room must also be noted.

One of the inconveniences of the hydrostatic method lies in the size of the corrections to be made for a variation in temperature of the water-bath, *e.* g., a variation of 0.14° with a volume of 1393 cc. leads to a correction of 0.034 g. In order to reduce these corrections as much as

[5] E. Saerens, *Bull. soc. chim. Belg.*, **33**, **28** (1924).

possible, we arranged to have the temperature of the bath close to that of the room. It must also be noted that the total volume of the bulb, sinker, net, etc., must be taken into account in these calculations. This volume is determined by the loss in weight of the bulbs fitted with the same equipment as at the moment of construction of the counterpoises.

The bulb is completely immersed in the bath and the capillary above the stopcock is filled with distilled water before immersion.

The weighings were done on a balance sensitive to one milligram. The suspension between water and air was made of a flexible copper wire 0.2 mm. in diameter; without taking special precautions, the measurements were easily reproducible to about one milligram.

One important source of error was due to bubbles of air which clung accidentally to the sides of the bulb; to prevent this the exterior surface was carefully freed from grease.

As an example of the calculation, the results on Bulb 15 are given.

Exterior volume of bulb, sinker, etc., 1385 cc.
Interior volume of bulb, 1161.4 cc.
Mean temperature of bath, 16.30".
Change in density of water per 0.01° in the region of 16.30°, 155×10^{-8}.

Weighing (a) Bulb filled with air, 68.437 g., bath at 16.31°
Correction for bath temp., $155 \times 10^{-8} \times 1 \times 1385 = 0.002$ g.
Corrected weight, 68.439 g.

Weighing (a') Bulb evacuated, 67.293 g., bath at 16.32°
Diff., (a) − (a') = 68.439 − 67.293 = 1.146 g.
True weight of air from weight (a) =

$$1161.4 \times 1.293 \times \frac{273}{273 + 16.4} \times \frac{737.7}{760} = 1.375 \text{ g.}$$

Loss due to contraction = 1.375 − 1.146 = 0.229 g.
Value corr. for density of water at 16.3° = 0.2292 cc.[6]
Contraction, corrected to 760 mm. = 0.236 cc.

Later we found

Weighing (b) Bulb filled with air, 68.455 g., bath at 16.32°
True weight of air =

$$1161.4 \times 1.293 \times \frac{273}{273 + 16.4} \times \frac{738.4}{760} = 1.376 \text{ g.}$$

Diff., (b) − (a') = 68.445 − 67.293 = 1.152 g.
Loss due to contraction = 1.376 − 1.152 = 0.224 g.
Corrected to 760 mm. = 0.2305 cc.

Weighing (b') Bulb evacuated, 67.295 g., bath at 16.32°
Diff., (b) − (b') = 68.445 − 67.295 = 1.150 g.
Loss due to contraction = 1.376 − 1.150 = 0.226 g.
Corrected to 760 mm. = 0.233 cc.

Mean contraction for the three measurements = 0.2332 *cc.*

For the six bulbs studied by this method the contraction has been determined by measurements (a), (a'), (b) and (b'), made in the same

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[6] This correction is negligible.

way. From the four measurements we get three values for the contraction, differing in the most unfavorable case by only 2.5% from the mean (Table II). We may say here that the values deduced from (b) and (b') are in all cases the closest to those obtained by Travers' method.

Travers' Method.—In this method the bulb is placed in a strong and rigid vessel, and the space between the bulb and the wall of the vessel is filled with water. The vessel is provided with a passage for the inlet tube of the bulb, and also for a vertical capillary filled with water. On evacuating the bulb, the water descends in the capillary owing to the diminution in the volume occupied by the bulb. We have already[7] described the method of operation in our first experiments. We could not then obtain a steady meniscus; what is more, the readings on contraction did not agree with those on expansion. We thought that the precision of the thermostat might play a role in this discrepancy, so our first effort was to employ a more sensitive thermostat;[8] during the new measurements, the temperature variations from the mean were about 0.002°. The dead space being 7 liters, and assuming a variation in the interior of the vessel of 0.001°, the displacement possible in the capillary would be

$$7 \times 10^6 \times 2 \times 10^{-7} = 1.4\ \text{mm.}^3$$

which is the order of precision desired in these measurements.

The cover of the vessel this time was curved and had a neck pointing up, larger on top than bottom. This was the manner of filling: the cover is fitted, in addition to the experimental bulb, with the calibrated capillary tube T, (see Fig. 1), and also a tube, H, with stopcock. The cylindrical vessel, placed in the thermostat, is filled with air-free distilled water to such a height that, on putting on the cover with bulb attached, the water does not quite reach the ground surface. Two weights, P, of 500 *g.* are tied to the stopcock in order to counterbalance approximately the buoyancy of the bulb. The cover is then closed tightly, taking care that the lubricant is evenly spread. Weights are placed on the cover so as to compensate largely for the buoyancy of the bulb.

First the bulb is evacuated[9] and then, by means of the tube, H, the space above the water in the cylinder. Due to the difference of pressure, air-free distilled water can then be slowly introduced through the capillary, T, until the space beneath the cover is almost filled. It is left under vacuum for a quarter of an hour, shaken lightly to detach bubbles from the bulb, then filled completely and the stopcock, L, closed. The distilled water used to fill the cylinder is stored in an auxiliary thermostat, maintained 0.2" higher than the thermostat used in the measurements, so as to compensate approxi-

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[7] Ref. 3, p. 667.

[8] L. Maricq and M. Beckers, Bull. *soc. chim. Belg.*, **37**, 12 (1928).

[9] To prevent the plug leaving the barrel of the stopcock when the space above the water containing the bulb is evacuated.

mately for the lowering of temperature caused by evaporation in *vacuo.* After two hours the meniscus in the capillary is constant to about 1 mm.^{3} After this lapse of time, all of the small bubbles in the apparatus are dissolved.

In our first experiments we did not succeed in preventing a rapid descent of water in the capillary. After various trials, we became sure that this difficulty was due to a slow rise of the cover as a result of the pressure of the water in the capillary, which was placed vertically. For, if the capillary has a length of 50 cm., the pressure is 50 g./cm.^{2}. The cover having a surface of about 300 cm.^{2}, it would take 50 g. × 300 = 15 kg. to balance this force. Obviously it is necessary to avoid the slightest movement of the cover, for it would require a rise of only $^1/_{25}\ \mu$ to cause a displacement of 1 mm.^{3} in the capillary. To lessen as much as possible the pressure produced by the water in the capillary, we bent the tube above the neck so as to render it nearly horizontal, thus reducing the pressure to a few cm. of water. In all our measurements the cover was held down by 10 kg. distributed equally over the surface.

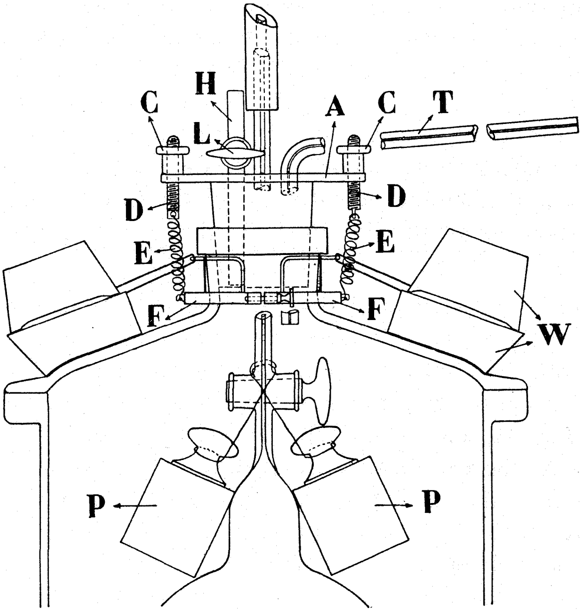

Fig. 1.

From the time this artifice was used, we were able to hold the level constant in the capillary; but, in the first experiments, it slowly dropped during the measurements. Later we were able to complete a series of experiments during each of which the level remained constant within 1 or 2 mm.^{3} from the beginning to the end of the measurement, i. e., for several hours. This difference of behavior can only be attributed to acquired skill in manipulating. For lubricating the ground joint we used anhydrous lanolin, which appeared to have the strongest adhesion.

To fasten the bulb and the other attachments to the cover, we tried two procedures. (1) A round disk of rubber with three holes was fixed in the neck and then covered with melted beeswax. In spite of all precautions, the wax cracked as it cooled, and even if one managed to cool it in one piece, it finally detached itself from the neck, as a result of the contraction on cooling. We had to abandon this method.

(2) A three-holed rubber stopper was solidly fixed in the cover as follows: a heavy metal plate, A, pierced also with three equally spaced holes, was placed above the stopper, B, and held tightly against it by three nuts, C, acting on threaded rods, D, flattened on one side. These screws are connected by means of springs, E, with a collar, F (in two pieces), which is rigidly attached to the neck of the cover by two screws. One could thus attain a progressive compression of the stopper, but, in spite of its strength, the stopper contracted slightly under an auxiliary pressure of 100 g. However, the level in the capillary came back very exactly as soon as this auxiliary pressure was removed. If any secondary action on the stopper is avoided, the level in the capillary remains very constant during a whole experiment, as we have already said. We may cite, by way of example, the results obtained with bulb No. 15; the level in the capillary decreased slightly during the experiment, and corresponding corrections have been made to the readings.

TABLE I

CONTRACTION AND EXPANSION DATA

Atmospheric pressure = 758.3 mm.

Contraction	0.2331	0.2343	0.2355	0.2343	0.2323	0.2331	Mean, 0.2338
Expansion	2331	2375	2351	,2343	.2319	.2331	Mean, ,2341

Mean of the two series, 0.2340 cc. Contraction corrected to 760 mm., 0.2345 cc.

The mean of the values obtained on contraction and on expansion do not differ as a rule by more than 0.2%, although in a few cases they reach 0.4%.

Concordance of the Two Methods.—This is shown by the following figures for six bulbs.

TABLE II

CONCORDANCE OF TWO METHODS

Bulb	Vol., cc.	Contraction obs., cc. Hydrostatic	Contraction obs., cc. Travers	Mean contr., cc.	Dev. from mean, %
6	906	0.1412	0.1330	0.1371	2.9
15	1161	,2332	.2345	2337	0 3
16	1176	.2593	2661	.2627	1 3
17	1165	.304	.3121	.308	1.3
12	2159	.3738	.3922	.383	2 4
13	2146	.374	3836	3788	1 3

It follows that the mean value of the two methods does not differ from the values obtained from either by more than 2%. We may therefore be permitted to conclude that the values obtained by each method may be considered correct to within 2%.

The hydrostatic method seemed to offer chances for more important accidental errors than that of Travers, so that henceforth we will only consider the results obtained by this latter method.

There follows a table showing the contractions found by the method of Travers, and also the values of η and K in the formula proposed by Moles and Miravalles

$$\eta = \frac{KV}{w} 10^{-3} \text{ cc.}$$

where η is the compressibility of the bulb under one atm., reduced to one liter, V is the volume in cc., w is the weight of the glass (minus that of the stopcock), and K is a constant, equal to 15.5, according to the authors.

TABLE III

CONTRACTION DATA

Bulb	Vol., cc.	Wt. of glass (minus wt. of the stopcock), g.	Obs. contr. reduced to 760 mm.	η	$K = \eta \frac{w}{V}$
3	609	70	0.0867	0.1423	16.4
4	624	56	.1178	.1890	17.0
5	630	71	.0884	.1403	15 8
6	906	101	.1330	.1468	16.4
7	910	113.5	.1160	.1275	16.0
8	1158	110	.2210	.1909	18.1
9	1174	93	.2758	.2351	18.6
10	1264	106	,2852	.2255	18.9
11	2162	143.5	.5287	.2446	16.2
12	2159	186	.3922	.1817	15.6
13	2146	192.5	.3836	.1788	16.0
15	1161	103	.2345	.2019	17.9
16	1176	89	.2661	.2264	17.1
17	1165	80	.3121	.2678	18.4
18	778	133	.0743	.0955	16.3
19	794	142	.0735	.0980	17.6
20	785	142	.0714	.0909	16.4
				Mean	17.0

The mean value of K is 17.0, with a maximum experimental deviation of 11%, and a deviation of 10% from the value 15.5 proposed by Moles and Miravalles. We should point out that the mean value of K found for the three bulbs of two-liter capacity is 15.9. The low value for these three (11, 12, 13) is due to the necks of the bulbs being only one cm. long, while all the others were about 4 cm. long. If these latter had also been made with short necks, thus diminishing the weight of glass, K would have been lowered by 5 or 10%, and thus would have approached considerably nearer the value of Moles and Miravalles.

Our experiments lead us to the following conclusion. The contraction under vacuum of bulbs of capacity from 600 to 2200 cc., and whose wall thickness varies appreciably, can be represented to within a few per cent. by the empirical formula

$$\eta = K \times \frac{V}{w} \times 10^{-3}$$

in which K has a value of about 16.0, if, in establishing the weight, a deduction is made for the neck of the bulb.

Our results thus correspond with those of Moles and Miravalles and confirm these authors in the opinion they have expressed, thus: "From the preceding, it necessarily follows that the empirical formula we have established gives the values of the compressibility of density bulbs more exactly than those measured by the authors, by a single method, and without taking excessive precautions."

The values obtained for Bulbs 3 to 10 of the preceding determinations diverge markedly from those considered above. We have repeated the calculations of these results, and have recalibrated the capillaries used. This has led us to make only a few small corrections to the old numbers. We give in the following table the corrected old values, new values and the concordance between the two.

TABLE IV

VALUES FOR BULBS 3–10

Bulb	Atm. press. during expt., mm.	Old values		New values	Ratio, new:old values
		Contraction in cc. corr. to 760 mm.			
3	766	0.067		0.0867	1.30
4	751	.0845		.1178	1.395
5	738	.065		.0884	1.36
6	745	.099	0.0955	.1330	1.39
	770	.092			
7	749	.0847	0.085	.1160	1.36
	763	.0855			
8	763	.1555		.2210	1.42
9	766	.1885		.2758	1.46
10	753	.2005	0.198	.2852	1.44
	769	.196			

Leaving out Bulb 3, the mean value of the ratios in the last column is 1.403, and it would require a diminution of the contraction of Bulb **3** by only 0.004 cc. to bring this also to the 1.4 ratio.

The remarkable constancy of this ratio of new to old values, in spite of its great sensitivity to small variations of the value obtained for the contraction, leads logically to the admission of some systematic error in our first measurements. The thorough examination to which we have subjected them ourselves did not lead us to discover it.

It seems difficult to attribute this to the fact that in our older measurements the water surrounding the bulb had not been freed from air. Whatever the cause may be we must admit that our first experiments are in error due to imperfection of the technique. It is to these same causes, so it seems, that the erroneous values obtained in this field by most investigators are due.[10] Fortunately, they do not introduce any large error into the gas density; in the case of butane, for instance, the density should be corrected by about one part in 20,000.

Variation of the Contraction as a Function of the Pressure.—In the determination of the density of a gas under reduced pressure ($^1/_3$ to $^2/_3$ atm.) it is necessary to know the contraction of the bulb with the same relative precision as under a pressure of one atmosphere. Until now one has been forced to accept the hypothesis that the contraction was a linear function of the pressure difference to which the bulb was subjected.[11] We wished to make an experimental verification of this hypothesis. Our measurements, by the Travers method, were carried out on three bulbs, on two of which the contraction under $^1/_3$ atm. was measured, and on the other at $^2/_3$ atm.

Our results are, in the three cases, completely in accord with the hypothesis advanced. The table shows the results obtained on Bulb 13.

TABLE: V

RESULTS ON BULB 13

Interior volume of the bulb, 2146 cc. Contraction reduced to 760 mm , 0.3836 cc.

Red. press., mm.	Values obtained in cc. On contraction	On expansion	Mean value	Calcd. value
479.4	0.2408	. . .	0 2408	0.2416
483.3	,2421	0,2443	.2432	.2436
479.9	.2411	.2411	,2411	.2419
477.6	.2399	.2399	.2399	.2407

To M. Timmermans, who has accepted the direction of our researches, we would like to express here our sincere gratitude for his aid and his willing support.

Summary

The contraction of density globes on evacuation has been investigated in connection with a physicochemical examination of easily liquefied saturated hydrocarbons. A hydrostatic method of measurement has been applied to the problem, as well as the method of Travers; the results by both methods are in good agreement.

The empirical equation proposed by Moles and Miravalles for the calculation of the compressibility of density globes is given additional confirmation by the results of the measurements.

Data have been obtained which lend support to the hypothesis that the

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[10] Ref. 4, p. 8.

[11] G. Baume, *J. chim. phys.*, 6, 18 (1908).

contraction of density globes is a linear function of the pressure difference to which the bulb is submitted.

BRUSSELS, BELGIUM

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. V. THE ATOMIC POLARIZATION

BY C. P. SMYTH

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In previous communications[1] the total polarization, P, of a substance has been divided into three parts, P_E, the electronic polarization, P_A, the atomic polarization and P_M, the orientation polarization due to the permanent moments of the molecules. This series of papers is concerned mainly with the conclusions to be derived from the values of P_M for liquids, but, as P_M is commonly obtained from the total polarization, P, by subtracting P_E and P_A, it is evident that no treatment of the problem can be complete without consideration of the two latter quantities. As P_E is discussed in another paper,[2] the present treatment will be confined to the significance of P_A, especially in its relation to molecular structure.

The polarization is commonly obtained from dielectric constants measured at frequencies up to 3,000,000 cycles or wave lengths down to 100 meters. For much higher frequencies or shorter wave lengths, the orientation of the dipoles in an applied field often becomes less and P_M diminishes, being negligible for frequencies in the infra-red region. In the range of visible light the frequency of the alternating field is so great that, for the most part, the electrons only are affected by it, the polarization being P_E alone. P_E is thus determined as the molar refraction for visible light. In the absence of anomalous dispersion, the small variation of P_E with wave length may be calculated by a simple dispersion formula such as that of Cauchy or Sellmeier[3] and the value of P_E obtained for the comparatively low frequencies, virtually infinite wave length, at which the dielectric constant is measured. However, the presence of oscillators with frequencies in the infra-red region causes anomalous dispersion and, in consequence, polarizations greater than the values obtained by extrapolation with the simple formulas. Actually these oscillators are displaced in the electric field, forming electric doublets and thus contributing to the polarization of the medium. Although some of these oscillators may be electrons, the majority are atoms, ions or radicals and, for this reason, their contribution

[1] (a) Smyth, Morgan and Boyce, THIS JOURNAL, 50, 1536 (1928); (b) Smyth and Morgan, *ibid.*, 50, 1547 (1928); (c) Smyth and Stoops, *ibid.*, 50, 1883 (1928).

[2] Smyth, Engel and Wilson, THIS JOURNAL, 51, 1736 (1929).

[3] See Errera, "Polarisation Diélectrique," Les Presses Universitaires de France, Paris, 1928; also Smyth, *Phil. Mag.*, 45, 849 (1923).

to the total polarization is termed the "atomic polarization" and designated by P_A. P_A is usually so small and difficult to determine with accuracy[4] that any attempt to subdivide it into the contributions of atoms, radicals, ions, etc., seems rather futile in the present state of our knowledge.

Since $P = P_E + P_A + P_M$ and P and P_E can always be determined, P_A is obtained by difference when P_M is known. P_M can be calculated from the temperature variation of the polarization of a gas or of dilute solutions, from which the polarization at infinite dilution can be obtained From measurements of dielectric constant[1b,5] in the solid state at temperatures sufficiently low and frequencies sufficiently high to prevent all orientation of the dipoles in the alternating field, a value can be obtained for the polarization from which P_M is eliminated, so that P_A can be obtained by subtracting P_E.[4,6]

Errera[3] has assembled a considerable number of values of P_A from the literature, calculating several not previously known. These are regrouped in Table I together with new values calculated by the writer and others taken from the literature. The values of the electric moment of the molecule, μ, are shown in order that it may be ascertained whether there is any connection between μ and P_A. For the gases, $P_E + P_A$ is determined from the temperature variation of the dielectric constant and P_A then obtained by subtracting P_E. A similar method is employed for $CHCl_3$, C_4H_9Cl, C_2H_5Br, C_4H_9Br, C_2H_5I and C_6H_5Cl, the substances being measured in solution. For the liquids without moment, P_A is determined by subtracting P_E from P, and for the majority of those with moment by subtracting P_E for the liquid from P for the solid. A small error in these calculations is caused by the fact that the value of P_E for the liquid may often be slightly different from those for the solid and the vapor, which are usually unknown. In the case of liquids for which μ is given as 0, it is sometimes impossible to distinguish between a very small value of μ and 0, which means that P_M may have a small finite value, instead of 0. This would, of course, cause a small error in P_A. As, in general, P_A is determined as a small difference between relatively large quantities, all the errors of experiment and method are accumulated in its values. A number of values obtainable from the literature, in particular several for vapors, are obviously so much in error that they are excluded from Table I, and the decimal places for many have been rounded off. The literature sources from which the values of μ and P_A have been obtained are indicated by the numbers following their values. Where no number is given after P_A, the value has been calculated by the writer from the data used in obtaining μ

[4] Cf. Ebert, Z. *physik. Chem.*, 113, 1 (1924).

[5] Debye, "Handbuch der Radiologie (Marx)," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1925, Vol. VI, p. 619.

[6] Errera, *Bull. sci. acad.* **roy.** Belg., [5]12, 327 (1926).

and the refractive indices in Landolt-Bornstein or "International Critical Tables."

TABLE I

ELECTRIC MOMENTS AND ATOMIC POLARIZATIONS

	$\mu \times 10^{18}$	P_A
HCl	1.03 (1)	1.2 (2)
HBr	0.79 (1)	0.2 (2)
HI	.38 (1)	.7 (2)
A	0 (3)	.1 (2)
N_2	0 (5)	0 (6)
NH_3	1.44 (4)	.5 (2)
O_2	0 (5)	0 (5)
CO	0.10 (6)	.1 (2)
CO_2	0 (7, 6)	0 (2)
CS_2	0.33 (6)	.9 (vapor)
SO_2	1.61 (4)	.9 (2)
CH_4	0 (8)	.8 (2)
C_2H_6	0 (9)	0 (2)
C_2H_4	0 (9)	.4 (2)
C_2H_2	0 (9)	1.9 (2)
n-C_6H_{14}	0 (10)	0.65 (10)
n-C_7H_{16}	0 (11)	.88 (11)
2,2-Dimethylpentane	0 (11)	.91 (11)
2,4-Dimethylpentane	0 (11)	.96 (11)
2-Methylhexane	0 (11)	.92 (11)
3-Methylhexane	0 (11)	.83 (11)
2,2,3-Trimethylbutane	0 (11)	.78 (11)
3,3-Dimethylpentane	0 (11)	.90 (11)
2,3-Dimethylpentane	0 (11)	.88 (11)
3-Ethylpentane	0 (11)	.76 (11)
2,2,4-Trimethylpentane	0 (11)	1.09 (11)
CH_3Cl	1.59 (24)	(4)
CH_2Cl_2	1.59 (8)	2.4
$CHCl_3$	1.05 (10)	6.2 (vapor) (12) 5.8 (liquid) (10) 6.0 (solid) (13) 3.0 (solid) (2)
CCl_4	0 (8)	3.0 (2)
$TiCl_4$	0 (14)	5.7 (2)
$SnCl_4$	0 (14)	10.6 (2)
C_2H_5Cl	1.98 (24)	(5)
C_4H_9Cl	1.89 (15)	5.4
C_2H_5Br	1.86 (10)	(11) (10)
CH_3I	1.62 (25)	(25) (vapor)
C_2H_5I	1.66 (16, 25)	(28) (vapor) 12 (liquid)
$CH_2{=}CCl_2$	1.18 (2)	2.8 (2)
cis-$CHCl{=}CHCl$	1.85 (2)	3.4 (2)
trans-$CHCl{=}CHCl$	0 (2)	3.2 (2)
cis-$CHCl{=}CHBr$	1.54 (2)	3.6 (2)
trans-$CHCl{=}CHBr$	0 (2)	3.5 (2)

TABLE I (Concluded)

	$\mu \times 10^{18}$	P_A
cis-CHBr=CHBr	1.22 (2)	5.3 (2)
trans-CHBr=CHBr	0 (2)	4.8 (2)
cis-CHI=CHI	0.75 (2)	8.0 (2)
trans-CHI=CHI	0 (2)	5.6 (2)
Cyclohexane	0 (2)	0.74 (2)
Benzene	0 (17)	1.5 (2)
p-$C_6H_4(CH_3)_2$	0 (18, 19)	2.1 (2)
$C_6H_5NO_2$	3.9 (19)	8 (2)
C_6H_5Cl	1.52 (10)	3.3 (10)
o-$C_6H_4Cl_2$	2.25 (20)	5.8 (2)
m-$C_6H_4Cl_2$	1.48 (20)	4.4 (2)
p-$C_6H_4Cl_2$	0 (2, 20)	3 (2)
o-$C_6H_4Br_2$	1.67 (2)	3.8 (2)
m-$C_6H_4Br_2$	1.22 (2)	2.2 (2)
o-$C_6H_4I_2$	1.63 (2)	1.3 (2)
H_2O	1.79 (21)	5.3 (vapor) (2) 2.0 (solid) (2)
H_2S	0.93 (6)	<1.5
CH_3OH	1.64 (22)	4.9 (13)
C_2H_5OH	1.74 (22)	5 (2)
$(CH_3)_2O$	1.29 (21)	2.2 (21)
$(C_2H_5)_2O$	1.14 (21)	3.9 (21)
$(CH_3)_2SO_4$	3.27 (2)	33.4 (2)
Cane sugar	......	24.8 (23)
Citric acid	......	28.4 (23)

(1) Zahn, Phys. Rev., 24, 400 (1924); (2) Errera, "Polarisation Diélectrique," Les Presses Universitaires de France, Paris, 1928; (3) von Braunmuhl, Physik. Z., 28, 141 (1928); (4) Zahn, Phys. Rev., 27, 455 (1927); (5) Calculated from (6); (6) Zahn and Miles, Phys. Rev., 32,497 (1928); (7) Stuart, *Z.* Physik, 47,457 (1928); (8) Singer, Physik. Z., 27, 556 (1926); (9) Smyth and Zahn, THIS JOURNAL, 47, 2501 (1925); (10) Smyth and Morgan, ibid., 50, 1547 (1928); (11) Smyth and Stoops, *ibid.*, 50, 1883 (1928); (12) Calculated by Errera from (8); (13) Ebert, Z. *physik.* Chem., 113, 1 (1924); (14) Calculated from results of Errera; (15) Unpublished work of Mr. H. E. Rogers; (16) Unpublished work of Dr. W. N. Stoops; (17) Sänger, *Physik.* Z., 27, 165 (1926); (18) Smyth, THIS JOURNAL, 46, 2151 (1924); (19) Williams, Physik. Z., 29, 174 (1928); (20) Smyth, Morgan and Boyce, THIS JOURNAL, 50, 1536 (1928); (21) Stuart, Z. Physik, 51, 490 (1928); (22) Stranathan, Phys. Rev., 31, 653 (1928); (23) Ebert, Z. physik. Chem., 114, 430 (1925); (24) Sircar, Indian J. Phys., 12, 197 (1928); (25) Mahanti and Sen Gupta, ibid., 12, 191 (1928).

Van Vleck[7] has calculated from infra-red intensity measurements that the vibrational polarization, which is P_A, is negligibly small for HCl, HBr, CO, CO_2, NH_3 and CH_4 and attributes to experimental error the difference found between the extrapolated refraction and the total induced polarization. He indicates, however, that this does not necessarily mean that, in other kinds of molecules, there may not be infra-red vibrational or electronic bands of such large amplitude, high effective charge or low frequency

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[7] Van Vleck, Phys. Rev., 30, 31 (1927).

as to cause a difference between the extrapolated refraction and the total induced polarization, thereby giving significant values for P_A. There appears to be reasonable doubt as to whether the value 1.2 of P_A for hydrogen chloride can be due in the main to experimental error, and this is true also of the value 0.9 for sulfur dioxide and especially of the value 1.9 for acetylene. However, the values for argon, nitrogen, oxygen and ethane are virtually 0, and that for ethylene, 0.37, differs from 0 by no more than the probable error. At this point one may inquire whether P_A, which is obtained usually as a small difference between relatively large quantities, really exists as a quantity of significant size or whether it appears merely as the result of the combined errors of P, P_E and P_M. The question may be answered by pointing to the fact that, except in the case of a very few results obtained from notably inaccurate measurements, experiment yields no negative values for P_A.

Since P_A is due to electrical dissymmetry caused by the displacement of atomic nuclei or groups within the molecule, one would expect it to be greater, the greater the number of the nuclei or groups in the molecule. Some evidence of such an increase is given by the paraffins in Table I. The possible error in P_A for methane is so large that this value has little significance and P_A for ethane is very small. The values for hexane, the nine isomers of heptane and the octane, 2,2,4-trimethylpentane, are obtained from measurements of P and P_E carried out with care upon the same samples of material. The temperature variation of P for five of these substances leads to the belief that P_M may be taken as 0 for all of them. The values of P_A thus obtained as $P-P_E$ should be more accurately comparable with one another than the others in the table. Although P_A for the heptane isomers varies somewhat with the structure, it is evident that there is an increase in passing from hexane to heptane to octane. A more striking increase of P_A with increase in the number of nuclei or groups is brought out by comparison of the value 28.4 for cane sugar with that of 5 for ethyl alcohol. Ebert[4] has calculated that each mole of water of hydration in $Na_2CO_3 \cdot 10H_2O$ contributes 4.75 to the value of P_A, each mole in $BaCl_2 \cdot 2H_2O$, 4.25, and each mole in $CuSO_4 \cdot 5H_2O$, 4.06, which shows a definite dependence of P_A upon the number of nuclei.

Since P_A depends upon the displacement of the nuclei or groups in the molecule, it should depend upon the forces binding these nuclei or groups, that is, the valence forces. Bates and Andrews[8] have used thermal data to calculate the force necessary to pull apart two atoms from their positions of equilibrium, and have obtained results which are of the same order of magnitude as the approximate values calculated by the writer[9] from molar

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[8] *Bates and Andrews, Proc. Nat. Acad. Sci., 14, 124* **(1928);** *Andrews,* ***Chem. Rev.,*** **5, 533 (1928).**

[9] Smyth, *Phil. Mag., 50, 361 (1925).*

refractions for the forces necessary to displace bonding electrons from their normal locations. In many cases where the actual forces cannot be calculated from the refractions, an idea of their relative magnitudes can be obtained from the refractions calculated for the electron groups. In this way, it is indicated that the C–O and H–O bonds are probably more rigid than the C–C and C–H bonds, in spite of which the values of P_A for the alcohols and ethers are larger than those for the paraffins. Although the values of P_A obtained for water by different methods do not agree well with one another, the correct value is almost certainly higher than that for hydrogen sulfide, while the refractions indicate that the forces of linkage are stronger in the water molecule. On the other hand, the forces linking carbon to halogen are lower than the C–C and C–H forces and the values of P_A for the compounds containing halogens are higher than those for the hydrocarbons. The marked rise in P_A on passing from carbon tetrachloride to titanium tetrachloride to stannic chloride is consistent with the decrease in binding force indicated by the refractions, the refractions of the chlorides in stannic chloride being almost those of free chloride ions. The different behaviors of the acetylene dihalides and the dihalogenated benzenes cannot be explained in terms of these forces alone. It seems probable that the smaller forces required to bend rather than stretch bonds may play an important role, but our knowledge of these is at present very meager. In any event, it is evident that the forces which have been considered do not provide an adequate explanation of the differences in P_A.

It is possible that the small molecules like hydrogen chloride and sulfur dioxide, which have electric moments, have larger values of P_A than the small molecules without moments, but this is uncertain because of the small values of P_A and the large errors. It is certain, however, that many small molecules with moments have values of P_A smaller than those of large molecules without moments. The values of P_A for the chlorine-substituted methanes are not sufficiently accurate to permit of definite conclusions. One may say, however, that CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4 and also C_2H_5Cl and C_4H_9Cl have values of P_A of about the same size, considerably larger than those for the paraffins. It would appear that the presence of electric doublets in the molecule, even if they oppose and cancel one another to give zero moment to the molecule as in carbon tetrachloride, is conducive to higher values of P_A. The doublets are presumably larger in titanium tetrachloride and still larger in stannic chloride, although as they are symmetrically located in the molecules, the total moments are zero. The value of P_A for liquid ethyl bromide is very uncertain, and the negative value, -5, calculated for the vapor from the measurements of Mahanti and Sen Gupta and not included in Table I shows only the uncertainty of the measurements.[10] The values calculated for the vapors of methyl and ethyl

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[10] Mahanti and Sen Gupta, *Indian J. Phys.*, **12,** 191 (1928).

iodide from the measurements of the same investigators and shown in the table in parentheses merely indicate that P_A is probably large for these substances, being thus far in agreement with the high value for liquid ethyl iodide, which is more accurately determined. The reason for the abnormally high values for these substances and also for dimethyl sulfate, determined by a different method, is not apparent. It may be in part experimental error and in part the large doublets and small binding forces. There is evidently need of measurements upon the alkyl halides in the solid state.

Among the acetylene dihalides the czs-compound, which has a considerable moment, always has a value of P_A larger than that of the corresponding trans-compound, which has no moment, although P_A increases when chlorine is replaced by bromine and bromine by iodine, while the moment of the cis-compound decreases. Among the dihalogen-substituted benzenes the value of P_A decreases from the ortho to the meta to the para compounds, as the moment becomes smaller, and also decreases on passing from the chlorine to the bromine to the iodine compounds, in contrast to the increase among the acetylene dihalides. P_A for cyclohexane is about the same as that for the heptanes and differs from that for n-hexane by no more than the possible error. The value for benzene is a little larger and *p*-xylene, which contains two small opposed doublets where the methyl groups are attached, has a still larger P_A, but the difference between it and that for benzene lies within the possible error. When a considerable doublet is present, as in chlorobenzene, P_A is appreciably increased, and the large doublet in nitrobenzene causes a large value of P_A.

It may be concluded that P_A is not generally an additive quantity but that it tends to be greater, the greater the number of atomic nuclei or groups in the molecule; probably, also, the smaller the forces binding these nuclei or groups, the greater the number of the electric doublets in the molecule and the more unsymmetrical the arrangement of these doublets in the molecule. However, unknown factors make it difficult to explain many of the differences found between different types of molecules.

Small changes in P_E have been found to accompany change of state and change of temperature,[2] but similar changes in P_A would have to be very large to be apparent, because of the relatively large errors involved. Thus, for chloroform the values obtained from the work of two different investigators for the solid differ from one another far more than do those for the vapor and the liquid and one of those for the solid. For water the best value for the solid is much lower than the value for the vapor, but other values for the solid not listed are close to that for the vapor. One can conclude only that the variation of P_A with temperature and change of state is less than the error usually occurring in the determination of its value.

In the majority of the determinations of the electric moments of the molecules of substances in the liquid condition, P_A has been neglected entirely and P_M obtained as the difference between P and P_E. As the electric moment is calculated from the square root of P_M, the inclusion of P_A in the value of P_M usually increases the value of μ by little more than the possible error when P_M is large. Thus, inclusion of P_A with P_M in the calculation increases the value of μ for C_6H_5Cl by 0.05 X 10^{-18} and for o-$C_6H_4Cl_2$ by 0.06 $\times$ 10^{-18}. Williams and his collaborators[11] working at only one temperature have been compelled to disregard P_A and, instead of obtaining P_E by extrapolation to infinite wave length, have subtracted the molar refraction for the sodium D-line from P and calculated μ from the difference. As the molar refraction for the D-line is slightly larger than P_E for infinite wave length, this procedure reduces the error caused by the failure to subtract P_A. When P_M is small or zero, disregard of P_A may introduce a relatively large error into the value calculated for the moment. If, for p-$C_6H_4Cl_2$, the value of $P_A = 3.4$ is added to that of $P_M = 0$, the moment calculated from the sum, 3.4, is 0.45 $\times$ 10^{-18}, instead of zero, as given by the correct value $P_M = 0$. In certain calculations of the moment made by the writer, Table I, ref. 18, μ was calculated from the difference between P and P_E. In this way values of 0.20 X 10^{-18}, 0.23 X 10^{-18} and 0.43 $\times$ 10^{-18} were obtained for benzene, p-xylene and carbon tetrachloride, respectively, for which Table I shows zero values of μ and not inconsiderable values of P_A. It was recognized at the time that values of μ less than 0.4 $\times$ 10^{-18} were, in many cases, indistinguishable from zero by the method of calculation employed, but the calculation for p-$C_6H_4Cl_2$ given above shows that neglect of P_A may give a value of μ larger than 0.4 X 10^{-18} when it is really zero and, for an electrically symmetrical molecule possessing a larger value of P_A, like trans-CHI—CHI, the error in μ would be larger. It is evident that the value 0.13 X 10^{-18} for the chlorine molecule calculated by the author in the same paper merely shows the moment to be small, if not actually zero, and that the value 0.58 $\times$ 10^{-18} for the bromine molecule is probably high because of the neglect of P_A. The small difference between this and the value 0.40 X 10^{-18} recently found by Anderson[12] indicates that P_A is small for bromine.

It is evident that if the moment is high and the molecule is small and contains only one or two electric doublets, P_A may be disregarded in the calculation of μ without, as a rule, introducing serious error in the result. If, however, the moment is small and the molecule is large and contains several electric doublets, it is unsafe to neglect P_A in the calculation of the moment.

Summary

Values for the atomic polarization of a large number of substances have been calculated or taken from the literature.

[11] Williams, *Physik. Z.*, 29, 174 (1928).

[12] Anderson, *Proc. Phys. Soc.*, 40, 62 (1928).

The binding forces calculated by Bates and Andrews from thermal data and by the writer from refractions are found inadequate to account for the differences between the displacements of the different nuclei and groups in the molecules.

The atomic polarization is not generally an additive quantity, but tends to be greater, the greater the number of atomic nuclei or groups in the molecule, the greater the number of electric doublets and the more unsymmetrical the arrangement of these doublets in the molecule.

In the calculation of the electric moment of a molecule, the atomic polarization may be disregarded without risk of introducing appreciable error only when the moment is high and the molecule is small and contains but one or two electric doublets.

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THE PHOTOSENSITIZED AND PHOTOCHEMICAL DECOMPOSITION OF HYDRAZINE

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Perhaps the most important fact now necessary for a complete understanding of the manner in which reactions are brought about by light energy is a knowledge of the action produced directly upon its absorption by the molecule. Taylor[1] has proposed, as a generalization of the facts now known, to state a Second Law of Photochemistry as follows: "The absorption of light is a quantum process involving one quantum per absorbing molecule (or atom). The photochemical yield is determined by the thermal reactions of the system produced by the light absorption." The resultants of this sequence of secondary thermal reactions are determined by ordinary physicochemical methods. The nature of the quantum process presents a more difficult problem. It has been possible in many cases from a complete kinetic study of the reaction to set up a mechanism, based on a postulated primary process, which yields satisfactory agreement with experimental observations. The postulated primary process is then assumed to be that actually occurring. For conclusive evidence as to the primary light action we must turn to that on the optical side furnished directly by molecular spectra. Thus far it has been possible to correlate satisfactorily the nature of the absorption spectrum with a definite primary action only in cases involving diatomic molecules. Those more complex give spectra showing complicated band systems which resist analysis. As a result of

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[1] Taylor, "First Report of the Committee on Photochemistry of the Division of Chemistry of the National Research Council."

these two lines of approach the nature of the primary processes and the sequence of secondary reactions appear to be definitely established for several photochemical reactions. These are mainly those involving the halogens and hydrogen halides.

The photochemical decomposition of ammonia has been the subject of more or less exhaustive study.[2] No mechanism has as yet been derived for this reaction which is in complete agreement with experimental facts, nor has the primary process been established beyond question. The simple reaction of an activated ammonia molecule on collision with a normal one to yield nitrogen and hydrogen

$$NH_3' + NH_3 \longrightarrow N_2 + 3H_2$$

does not satisfactorily account for the low quantum yield at high pressures, nor the observation[3] that a rapid decomposition takes place at a pressure of 0.001 mm. of mercury. Photochemical decomposition should cease and fluorescence enter at this low pressure. The ultraviolet absorption bands of ammonia, also, do not show the fine structure ordinarily expected for cases where light absorption leads only to the activation of the molecule. Bates and Taylor[4] pointed out that a primary process of the type

$$NH_3' \longrightarrow N + H + H_2$$

proposed by Kuhn[5] is impossible if the recent values of the heats of dissociation of nitrogen and hydrogen molecules be accepted, and that his postulated secondary reactions are not consistent with several experimental facts.

From considerations involved in the facts that ammonia is decomposed by excited mercury atoms with an energy content of 112,000 calories and that the gaseous reaction products contain hydrogen in appreciable excess of the stoichiometric proportion N_2:$3H_2$, the above authors suggested that all molecules might undergo decomposition on light absorption, hydrazine formation being an intermediate stage. The proposed mechanism is

$$NH_3 + h\nu \longrightarrow NH_3' \tag{1}$$

followed by either

$$NH_3' + NH_3 \longrightarrow N_2H_4 + H_2 \tag{2}$$

or

$$NH_3' \longrightarrow NH_2 + H \tag{3}$$

$$NH_2 + NH_3 \longrightarrow N_2H_4 + H \tag{4}$$

$$NH_2 + H_2 \longrightarrow NH_3 + H \tag{5}$$

This would then be followed by secondary photochemical hydrazine decomposition, presumably into nitrogen and hydrogen. Such a mechanism,

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[2] For summary of data see Kistiakowsky, "Photochemical Processes," The Chemical Catalog Company, Inc., New York, **1928,** pp. 251–254.

[3] Bonhoeffer and Farkas, Z. *physik. Chem.*, **134,** 337 (1928).

[4] Bates and Taylor, THIS JOURNAL, 49, 2438 (1927).

[5] Kuhn, *Compt. rend.*, **177,** 956 (1923); 178, 708 (1924); *J. chim. phys.*, **23,** 521 (1926).

although more satisfactory than those previously advanced, does not account for several observations of earlier investigators.[2]

Under the above assumptions hydrazine decomposition would determine materially the characteristics of the ammonia decomposition. It was hoped that an investigation of the photochemical decomposition of hydrazine might lead to a removal of some of the difficulties in the case of ammonia. Hydrazine, while more complex than ammonia, offers a case of a solely nitrogen–hydrogen compound. Its behavior might then lead to a better understanding of the action of radiation upon the nitrogen to hydrogen linkage and perhaps increase our knowledge of such reactions in general.

Hydrazine has been found to be decomposed by ultraviolet light and by excited mercury more readily than ammonia. The results obtained do not support its formation as an intermediate stage in the ammonia decomposition. They do, however, favor a mechanism of the general type as that suggested by Bates and Taylor.

Experimental Method

Apparatus.—Preliminary experiments were made with the flow apparatus and mercury arc described by Bates and Taylor.4 The usual static system was employed throughout the remainder of the decomposition studies. This consisted of a quartz reaction chamber of about 150-cc. capacity joined by a quartz to pyrex seal and capillary tubing to a constant volume mercury manometer, oil pump and to a hydrazine reservoir through a three-way stopcock. The latter provided means for the admission of various other gases to the reaction chamber. A liquid-air trap in the vacuum line prevented contamination of the pump.

Temperature control was obtained by immersing the reaction vessel in a copper tank through which water was continuously flowing. The water was heated to any desired temperature by previous passage through electric heaters. In the sensitized experiments a large battery jar was substituted for the tank. In any case the temperature could be controlled to about one degree by proper variation of the temperature and rate of flow of the entering water. A stream of air gave efficient stirring.

The total radiation from a vertical Cooper–Hewitt mercury arc of the ordinary type provided the source of illumination. Light reached the reaction vessel through a quartz window in the copper tank. In the purely photochemical experiments the arc was run on 110 volts and 3.5 amperes, cooled only by an air blast. Its distance from the wall of the reaction vessel was about 2.0 cm. In the photosensitized experiments the arc was water cooled, being placed in the tank with the reaction vessel. It was run on 110 volts and 5.0 amperes, and its distance from the reaction vessel was varied from 0.5 cm. to 6 cm. For the sensitized study, which was made after the completion of the photochemical experiments, mercury vapor was supplied by about 0.5 cc. of mercury forced into the reaction vessel from the manometer.

In order to determine the relation of the reaction rate to the incident light intensity a metal frame containing a slit the width of the arc and half its length was soldered to the copper tank. The distance from slit to the quartz window was about 4 cm. Copper gauze screens of suitable dimensions and blackened by oxidation to cut down stray light served to vary the amount of light. reaching the reaction vessel These could be fixed rigidly in the metal frame between the slit and quartz window. Relative light intensities were measured with a Moll thermopile. A shutter controlled from the position of the galvanometer scale governed the admission of light to the vessel and to the thermopile. For these experiments the arc was placed in a water-bath separate from the reaction vessel and run at a constant temperature of 30° on 110 volts and 5.5 amperes. It was started by breaking down the space charge with a high tension coil so that its position was unchanged throughout the series.

The experiments on the thermal decomposition were carried out in the same system described above, the reaction vessel being surrounded by an electric furnace.

Preparation of Materials.—Hydrazine hydrate, $N_2H_4 \cdot H_2O$, was first prepared from Kahlbaum's C. P. hydrazine sulfate, $N_2H_4 \cdot H_2SO_4$.[6] A concentrated solution of the latter was mixed with the calculated amount of highly concentrated potassium hydroxide solution, an equal volume of alcohol added and the precipitated potassium sulfate removed. The mixture was then distilled up to 118° under ordinary pressure, decanted from a further precipitate of potassium sulfate and fractionated at 121–122 mm. pressure. An all-glass distillation apparatus was employed. The portions distilling between 73 and 74°, consisting of 85 to 97.5% of hydrazine hydrate, served for the preparation of anhydrous hydrazine.

The preparation of anhydrous hydrazine was carried out according to the method of Hale and Shetterly[7] with the modifications suggested by Welsh.[8] The all-glass apparatus described by the former authors was employed. The method consists, briefly, in dehydrating the hydrazine hydrate by refluxing for several hours with a large excess of barium monoxide and then distilling the hydrazine in an atmosphere of hydrogen at a pressure below 300 mm. of mercury. This method avoids action of the hydrazine on glass and has been shown to give a product containing 99.7% of hydrazine. A glass tube with a stopcock attached was sealed directly to the distillation apparatus and evacuated. The liquid hydrazine (b. p. 113.5°) was run into this from time to time during the distillation. It was then sealed off and fused to a second such reservoir attached to the reaction bulb. Contact with air was thus avoided. The hydrazine could then be freed from dissolved gases before use by isothermal distillation from the first container into the second. Dissolved ammonia was removed by evacuation at room temperature. The liquid hydrazine was preserved in *varuo* during the entire research. A sample of its vapor burned over copper oxide gave a pressure of nitrogen closely approximating the theoretical to be expected from a 100% sample of hydrazine. This result, together with the amount of pressure increase upon total decomposition and analysis of the decomposition products, renders the presence of an appreciable amount of the hydrate in the hydrazine vapor employed improbable.

Electrolytic hydrogen and nitrogen from cylinders were used. Hydrogen was purified over hot platinized asbestos and phosphorus pentoxide, and nitrogen pver hot copper turnings and phosphorus pentoxide. The ammonia gas employed was a carefully prepared sample stored in a cylinder over sodium.

Procedure.—Before each experiment the hydrazine container was carefully evacuated in case slight decomposition might have occurred by diffusion of the vapor up to the greased stopcock surface. The reaction system was flushed several times with the vapor. The reaction vessel was filled by allowing hydrazine to vaporize into it under its own vapor pressure at room temperature. The initial pressures thus obtained could be varied from about three to ten millimeters. The arc was then started and the reaction followed by noting the increase of pressure at suitable time intervals. An electric contact between a sealed-in tungsten wire and the mercury of the manometer

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[6] Gmelin-Kraut, "Handbuch der Anorganischen Chemie," 1925, Vol. 1, p. 193.

[7] Hale and Shetterly, THIS JOURNAL, 33, 1074 (1911).

[8] Welsh, *ibid.*, 37, 499 (1915).

allowed a delicate adjustment to constant volume. The manometer scale was so arranged that readings could be made to about 0.3 of a millimeter with a fair degree of accuracy. Numerous checks were made on all experiments.

Analysis of Reaction Products.—This could be carried out in the reaction system by means of a small side tube, attached as closely as possible to the quartz bulb and sealed to an electrically heated copper oxide tube through a stopcock. The method of analysis was briefly as follows. Hydrazine remaining after an experiment was first removed by surrounding the side tube with a carbon dioxide–ether freezing mixture, and ammonia determined by replacing this with liquid air. The gases non-condensable in liquid air (H_2 and N_2) were admitted to the copper oxide and the hydrogen burned, the water formed being simultaneously frozen out. The decreases in pressure thus obtained give the amounts of the various gases present; nitrogen was determined by difference. It was necessary to remove any residual hydrazine before admitting the gases to the copper oxide since it was found to reduce this latter in the cold, giving nitrogen and water.

The above method for separating ammonia from hydrazine vapor was shown to give accurate results by analyses of known mixtures of the two. It cannot be employed when the pressure of ammonia gas exceeds approximately 30 mm., the vapor pressure of liquid ammonia at the temperature of a carbon dioxide–ether mixture (–79°).

As carried out, this method of analysis offers the disadvantage that five to six hours are required for its completion. This is due to the slow diffusion of the gases to the freezing zone and the copper oxide. If many analyses are to be made it is desirable to arrange a means of circulating the gases through the system.

Photochemical Decomposition

Course of the Reaction and Products.—Upon illumination with the total radiation from the mercury arc, gaseous hydrazine undergoes decomposition. As will be later discussed, hydrazine vapor shows a marked light absorption in the ultraviolet below about 2400 Å. It is evident, therefore, that it is the portion of the mercury radiation below this wave length which is effective.

As the decomposition progresses the pressure in the system increases to a value three times that of the initial hydrazine,[9] after which no further change occurs. This tripling of the pressure indicates that the final reaction products are nitrogen and hydrogen only, hydrazine decomposition being complete. Analysis of the gaseous products at the end of the reaction confirms this. One experiment gave 64% of hydrogen and 36% of nitrogen, a second, 65% of hydrogen and 35% of nitrogen. The theoretical is 66.7% of hydrogen and 33.3% of nitrogen.

Hydrazine, however, does not decompose directly into the elementary constituents, but into ammonia, nitrogen and hydrogen according to the stoichiometric equation

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2 \qquad (1)$$

The ammonia subsequently decomposes photochemically into nitrogen and hydrogen

$$2NH_3 \longrightarrow N_2 + 3H_2 \qquad (2)$$

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[9] In several experiments slight overrunning of this three-fold value was obtained. This is undoubtedly to be attributed to traces of hydrazine condensed or adsorbed on the walls of the quartz vessel.

at a slower rate. These facts were ascertained by analysis of the gaseous products at various stages of the reaction. Ammonia was found present up to the end of the reaction. The ratio of ammonia to nitrogen and hydrogen decreased as the reaction proceeded. Table I gives the results of analyses made after varying amounts of decomposition. The initial pressures of hydrazine were constant to about 0.5 of a millimeter.

TABLE I

VARIATION OF COMPOSITION OF PRODUCTS WITH EXTENT OF DECOMPOSITION

Expt.	Press. of total prod., mm.	Press. of NH_3, mm.	Comp. of total products			Comp. non-condensed gases	
			NH_3, %	H_2, %	N_2, %	H_2, %	N_2, %
37	6.1	2.2	38	32	30	52	48
35	12.2	3.8	32	34	34	50	50(?)
38	13.4	4.2	31	39	30	56	44
36	16.2	5.1	31	38	31	55	45
39	24.1	1.8	8	55	37	60	40
28	26.5	<0.5	0	65	35	65	35
Theoretical for no decomp. of NH_3			50	25	25	50	50

As the table shows, the actual quantity of ammonia found in the products first increases and then decreases upon continued illumination. All ammonia finally disappears as the pressure attains a three-fold value.

On account of the fact that the rates of hydrazine and of ammonia decomposition are of the same relative order of magnitude, the two reactions could not be isolated in the photochemical experiments. The use of monochromatic light would not affect this since the two substances absorb in practically identical spectral regions. The maximum amount of ammonia obtained in any experiment corresponded to 77% of that to be expected from decomposition according to Equation 1. It will be seen later that a sharp separation was made in the sensitized experiments.

It is of interest to note that gaseous hydrogen azide (HN_3) is photochemically decomposed[10] by ultraviolet radiation from an aluminum spark. In this case, also, the products of the reaction are hydrogen, nitrogen and ammonia (ammonium azide). It is probable that the formation of ammonium azide, noticed on longer illumination, is the result of a secondary reaction between the ammonia produced and hydrogen azide

$$NH_3 + HN_3 \longrightarrow NH_4N_3$$

Rate of the Decomposition.—The photochemical decomposition of hydrazine is more rapid than that of ammonia. In Table II are given the data for a typical experiment. The rates in the last column are the average increases of pressure per minute taken over the intervals of time between manometer readings. It will be noticed that a definite change in rate occurs at a pressure approximately double that of the initial. The apparent constancy over successive periods is due to the method of averaging

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[10] Beckman and Dickinson, THIS JOURNAL, 50,1870 (1928).

and to the fact that pressure could not be read to less than several tenths of millimeter.

TABLE II

DATA FOR A TYPICAL EXPERIMENT

Initial $P_{N_2H_4}$ = 8.3 mm. Barometer 760.1 mm. Arc at 110 v. and 3.5 amps.

Time, min	*Press*, mm.	*Temp*, °C.	*Rate*, ave Δ*p*/min	Time, min.	*Press.*, mm.	*Temp.*, °C.	*Rate*, ave. Δ*p*/min.
0	8.3	24 1	0 2	77	20.3	25.C	.08
3	8.8	24 2	.2	98	21.9	25.0	
10	10.1	24 7	.2	125	22.3	25.6	.03
17	11.5	25.4	.2	150	23.6	25.2	
33	15.1	24.0	.2	190	24.2	25.1	.01
42	16 9	24.8	.2	230	24.5	24.3	
50	18.5	25.6	.07	295	24.6	24.1	
65	19.5	23 6	.07				

In Fig. 1 time of illumination is plotted against pressure increase for several representative experiments. Under the experimental conditions,

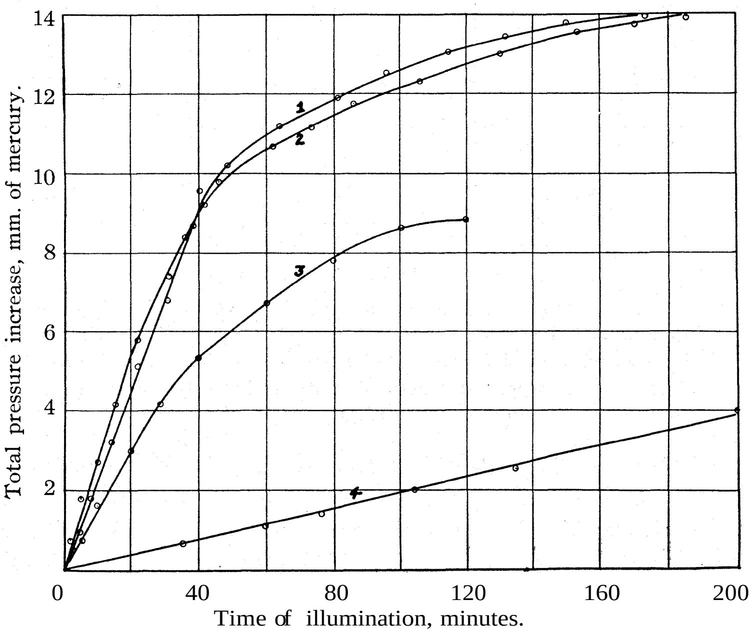

Fig. 1.—Rates of the photochemical decomposition. Curves 1, 2 and 3, hydrazine at initial pressures of 9.8 mm., 8.6 mm. and 4.3 mm., respectively. Curve 4, ammonia at an initial pressure of 14 mm.

doubling of the pressure generally occurred in thirty to forty minutes, tripling, in four to five hours. The initial hydrazine pressures varied from six to ten millimeters. The half-time values determined from the curves of Fig. 1 indicate the reaction to be unimolecular in character. The apparent unimolecularity is without meaning, since the pressures obtained are the resultants of those given by two reactions. A unimolecular reaction order is also to be expected if the light absorption is not nearly complete. The amount of light absorbed then becomes directly proportional to the concentration of reactant. The first portions of the rate curves are predominantly hydrazine decomposition, the last portions predominantly ammonia. It was impossible with the present experimental arrangement to vary the initial hydrazine pressure sufficiently to determine its effect, but the rate is approximately directly proportional to it (see Figs. 1 and 2).

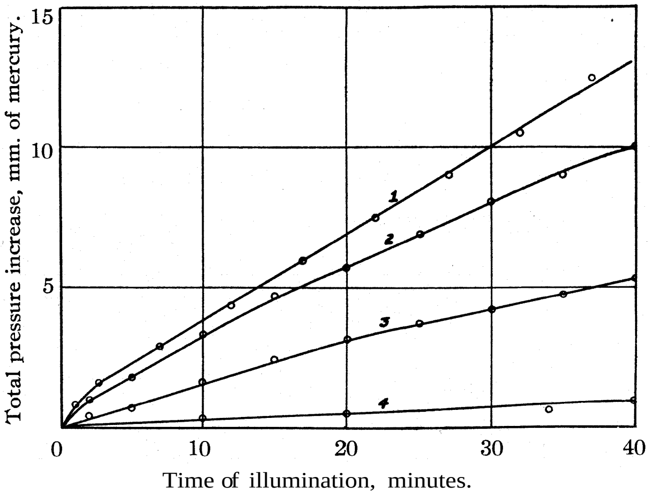

Fig. 2.—Rates of the photochemical decomposition for the first half of the total reaction. Curves 1, 2 and 3, hydrazine at initial pressures of 12.6 mm., 9.9 mm. and 4.3 mm., respectively. These curves represent practically entirely hydrazine decomposition. Curve 4, ammonia at initial pressure of 14 mm.

Temperature.—The rate of decomposition is independent of the temperature over the range studied, 15 to 45°. Experiments were made under practically identical conditions of illumination and hydrazine concentration, the only controllable variable being temperature. The increase in rate of ammonia decomposition in this temperature range is negligible.

Comparison of Hydrazine and Ammonia.—The rate of photochemical ammonia decomposition was investigated in the same system. The conditions of illumination and temperature were identical with those used in the hydrazine experiments. In Fig. 2 the rate curves for hydrazine, up to a doubling of the pressure, are plotted for experiments with conditions comparable to those where ammonia was studied. The ammonia curve is shown on Figs. 1 and 2. The curves given in Pig. 2 represent practically entirely hydrazine decomposition over the initial two-thirds, since ammonia decomposition is slow. Both hydrazine and ammonia curves may be taken'as straight lines without appreciable error. A comparison of the slopes, where the pressures are comparable, shows that the hydrazine reaction proceeds at ten times the rate of the ammonia reaction. This result is probably correct within 10%.

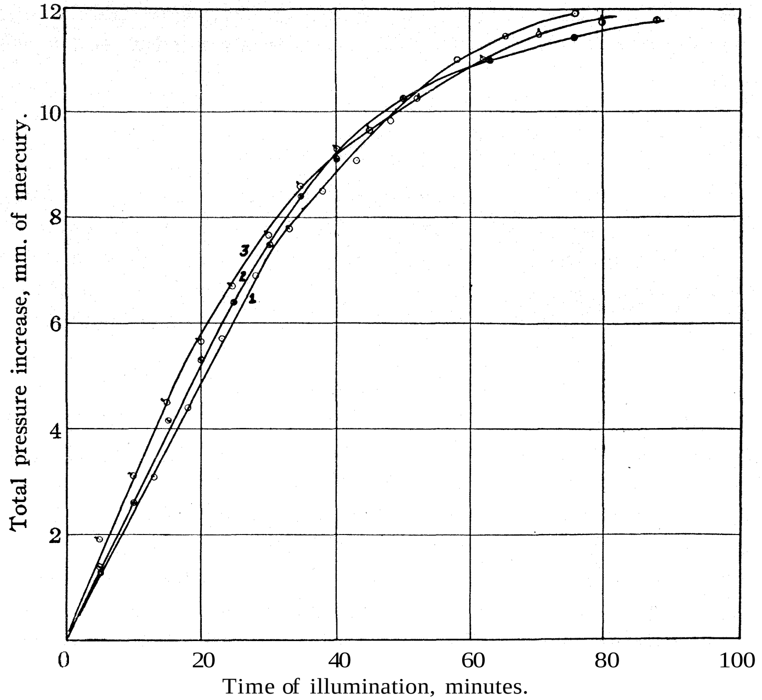

Fig. 3.—Effect of added gases on the rate of photochemical decomposition. Curve 1, hydrazine alone, initial pressure 8.9 mm. Curve 2, hydrazine with hydrogen present; pressure of hydrazine 8.6 mm., pressure of hydrogen, 8.0 mm. Curve 3, hydrazine with ammonia present; pressure of hydrazine 9.1 mm., pressure of ammonia 18.6 mm.

Effect of Added Gases.—Addition of nitrogen, hydrogen or ammonia to the hydrazine does not affect its rate of decomposition. Experiments were made in which these gases were added to hydrazine in concentrations up to twice its concentration. Fig. 3 contains rate curves for experiments with hydrazine alone and with ammonia and hydrogen present initially. The curves coincide within experimental error. Small variations from one experiment to another occurred with hydrazine alone. These may be attributed to small variations in the intensity of the arc and in initial hydrazine pressure. Ammonia decomposition is of course occurring simultaneously with that of hydrazine where ammonia is present, but the increase in rate due to this is negligible as compared with that of the latter.

Thermal Decomposition of Hydrazine

During the course of the photochemical experiments it was thought of interest to investigate the thermal decomposition of gaseous hydrazine since this could be accomplished readily in the same experimental system. It was found that in a quartz bulb hydrazine begins to decompose thermally at about 250°. The reaction products in this case were mainly ammonia and nitrogen in amount indicating decomposition according to the stoichiometric equation

$$3N_2H_4 \longrightarrow 4NH_3 + N_2 \qquad (3)$$

and not

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$$

as was found in the photochemical experiments. The compositions of the reaction products in two experiments were: (1) 71% of ammonia, 24% of nitrogen, 5% of hydrogen; and (2) 68% of ammonia, 26% of nitrogen and 6% of hydrogen; the theoretical on the basis of Equation **3** should be 80% of ammonia, 20% of nitrogen and no hydrogen. Consequently, a small amount of reaction takes place in such a manner as to yield hydrogen. Experiment showed no decomposition of ammonia in the quartz bulb in several hours at 500°. It may be noted that the pressure increase observed on total decomposition of a sample of hydrazine was approximately 5 to 3, which is that to be expected from Equation 3.

Since these results indicated a termolecular reaction order, Mr. Askey has carried out a kinetic investigation of the reaction in this Laboratory. His results[11] show that the thermal hydrazine decomposition is heterogeneous, taking place on the quartz surface, and is unimolecular in character. He has also found that on the surface of a heated platinum or tungsten wire the reaction occurs according to the same equation as photochemically.

Photosensitized Decomposition

When sensitized to light of 2537 Å. by mercury vapor, photochemical decomposition of hydrazine occurs. No decomposition takes place on standing in contact with mercury. The results of the sensitized studies are the most important obtained, since in this case the radiation is practically monochromatic, absorption undoubtedly complete and the concentration of the absorbing material unchanged as reaction proceeds. They enable us to formulate a mechanism for the reaction.

Reaction Products.—The decomposition of hydrazine by excited mercury atoms yields ammonia, nitrogen and hydrogen as products and takes place according to the stoichiometric equation

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$$

as does the purely photochemical reaction.

Several experiments were made with the flow system previously men-

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[11] Unpublished.

tioned.[4] Hydrazine vapor was passed through the arc, condensable products were removed with liquid air and the permanent gases analyzed. In one experiment these gave 47% of hydrogen and 53% of nitrogen; in a second, 48% of hydrogen and 52% of nitrogen. The theoretical for the above equation is 50% of hydrogen and 50% of nitrogen. The slight deficiency in hydrogen is undoubtedly to be ascribed to clean-up of atomic hydrogen on the walls.

When photosensitized by mercury vapor the rate of hydrazine decomposition so greatly exceeds that of ammonia that a nearly complete separation of the two reactions is possible. A very rapid increase in pressure ends when a doubling of the initial has been reached. This corresponds to complete hydrazine decomposition according to the above equation. Table III gives the results of analyses of the products made at this point.

TABLE III

COMPOSITION OF PRODUCTS FROM THE SENSITIZED REACTION

Expt.	Total products NH_3, %	 H_2, %	 N_2, %	Non-condensable gases H_2, %	 N_2, %
44	45	25	30	45	55
45	49	25	26	50	50
Calcd. for no NH_3 decomp.	50	25	25	50	50
Sensitized NH_3 decomposition				72	28

In another experiment where hydrogen was present initially 48% of ammonia was obtained. The quantity of ammonia found corresponds to 90 to 95% of the theoretical. The excess of nitrogen may be attributed to clean-up of hydrogen. Any error is magnified since nitrogen was obtained by difference. Dickinson and Mitchell[12] found 70% of hydrogen in the products of the sensitized decomposition of ammonia in a static system. Our value, 72%, checks this closely.

Rate of the Decomposition.—The decomposition of hydrazine is the most rapid reaction thus far obtained in this Laboratory with excited mercury. In Fig. 4 is plotted increase of pressure with time of illumination for several typical experiments. The temperature used was 30°. Increase of pressure proceeds rapidly to a point corresponding to a doubling of the initial and to complete hydrazine decomposition. As can be seen from the figure a very sharp break in the curves is evident at this point. Beyond, the pressure increases very slowly toward a three-fold value as decomposition of the ammonia formed proceeds. Ten millimeters of gaseous hydrazine are decomposed in less than three minutes with the arc at 5-mm. distance, in four minutes at 20 mm. and in twelve minutes at a distance of 60 mm. In later experiments the reaction rate was followed more readily by cutting down the light intensity with a blackened copper gauze screen.

Comparison of Hydrazine and Ammonia.—A curve for the rate of

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[12] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, 12, 692 (1926).

ammonia decomposition under identical conditions of mercury vapor concentration and illumination with resonance radiation is given on the same figure. The large difference in the rates for hydrazine and ammonia is evident. The curves for hydrazine and for ammonia are linear within experimental error. Comparison of their slopes, $\Delta p/\Delta t$, shows that hydrazine is decomposed at a rate forty times that of ammonia.

The illumination in the purely photochemical and in the sensitized experiments was only roughly the same, as no effort was made to keep it identical. Several experiments with mercury sensitization were made with the arc at a distance of 2 cm., approximately that in the photochemical. The increased intensity of the 2537 Å. line due to water cooling of the arc would be without appreciable influence on the photochemical reaction since hydrazine does not absorb in this spectral region. We may obtain, therefore, a rough estimate of the ratio of the rate of sensitized to photochemical decomposition by comparison of the slope of the curve for these experiments with that of the photochemical. This gives a value for the rate of the sensitized reaction 110 to 120 times the photochemical rate. This value is probably somewhat high since the arc was burning on a slightly

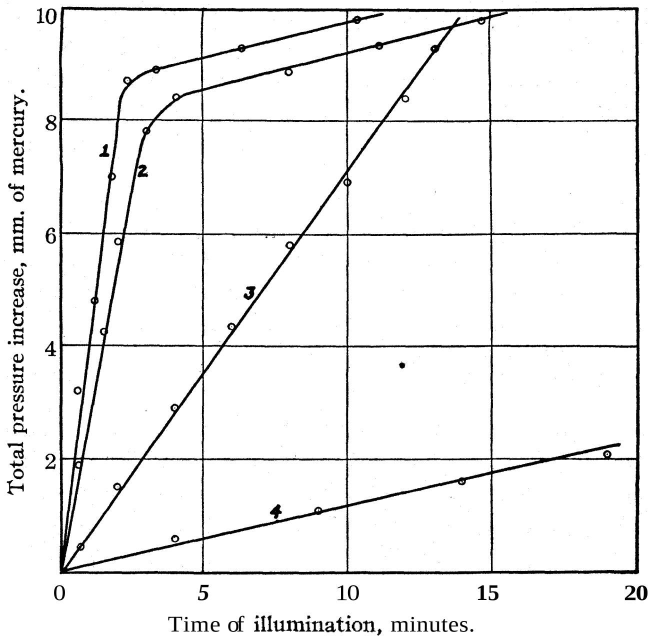

Fig. 4.—Rates of the photosensitized decomposition. Curves 1, 2 and 3, hydrazine; initial pressures 9.4 mm., 9.2 mm. and 10 mm., respectively; arc at distance of 0.5 cm., 2 cm. and 6 cm., respectively. Curve 4, ammonia, initial pressure 16 mm.; arc at distance of 0.5 cm.

higher wattage. From the preceding value we may also calculate that the ratio of sensitized to photochemical ammonia decomposition rate in these experiments is approximately 30 to 1.

Chain Mechanism and Quantum Efficiency.—In order to determine the quantum efficiency in the sensitized hydrazine decomposition, the mercury sensitized combination of hydrogen and oxygen was measured in

TABLE IV

COMPARISON OF RATES OF $H_2 + O_2$ REACTION AND N_2H_4 DECOMPOSITION

$2H_2 + O_2$			N_2H_4		
Time, min.	Press., mm.	Δp mm. per min.	Time, min.	Press., mm.	Δp mm. per min.
A. First Light Intensity					
Expt. 58. Satd. gases			Expt. 42		
0	329.4	2.8	0	9.4	4.0
10	301.6	2.6	2.2	18.1	
20	275.4	3.2	Expt. 45		
30	243.8	3.1	0	9.3	4.0
50	180.0	3.2	0.5	11.3	4.5
60	148.1	3.2	1.3	14.9	3.6
70	115.8		1.8	16.7	
Av. Δp/min. = 3.0. Mm.			Av. Δp/min. = 4.0. Mm.		
H_2O^a formed per min. = 2.0			N_2H_4 decomp. per min. = 4.0		
B. Second Light Intensity					
Expt. 62. Dry Gases			Expt. 61		
0	314.2	0.10	0	9.8	0.40
10	313.2	.11	3	11.0	.50
30	310.9	.14	6	12.5	.47
50	308.1	.11	13	15.8	.40
70	305.9	.13	18	17.8	
90	303.3		Av. Δp/min. = 0.45. Mm.		
Av. Δp/min. = 0.12. Mm.			N_2H_4 decomp. per min. = 0.45		
H_2O^b formed per min. = 0.24					
Expt. 63. Saturated gases					
0	293.3	0.32			
10	290.1	.35			
20	286.6	.40			
30	282.6	.38			
40	278.8	.40			
50	274.8	.40			
60	270.8				
Av. Δp/min. = 0.37. Mm.					
H_2O formed per min. = 0.25					

[a] With liquid water initially present in the reaction vessel the pressure decrease is the sum of that due to the volume change in the reaction and that due to condensation of water vapor formed; the rate of water formation is, therefore, $^2/_3$ of the total pressure decrease.

[b] Where dry gases were used the rate of water formation is given by twice the pressure decrease. The pressure increase gives directly the rate of N_2H_4 decomposition.

the same system. Mercury vapor concentration and illumination with resonance radiation were identical. Experiments were made with two light intensities. The ratio of hydrogen to oxygen was 2 to 1. It has been shown[13] that the rate of this reaction is independent of total pressure. The results obtained in these experiments are recorded in Table IV.

From the preceding table it is evident that the sensitized decomposition of hydrazine has a rate at least twice that of the combination of hydrogen and oxygen. The latter reaction proceeds through hydrogen peroxide formation,[14] it being possible to obtain practically quantitative yields of this substance by use of a flowing system. In a static system the hydrogen peroxide subsequently undergoes decomposition, the final product being water vapor. Using a flowing method Marshall[14] was able to show that sensitized hydrogen peroxide formation is a chain reaction with chains of at least 4.6 to 6.6 molecules. Since hydrogen peroxide decomposition is represented by the equation

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

the rate of water formation in the present experiments represents the rate of hydrogen peroxide formation. It is apparent, therefore, that hydrazine decomposition is a chain reaction involving chains at least twice as long as those in the former.

Quantum Efficiency.—With the entire arc cooled with water, the condition in our experiment, a value of 3.3 members was found by Marshall for the chain length and of 6.6 molecules for the quantum efficiency. On the basis of the number of molecules disappearing as indicated by pressure change, a calculation of the quantum efficiency in hydrazine decomposition, from the data of Marshall and that of Table IV, gives a value of 13 molecules *per* absorbed *quantum*. This figure may be regarded as a minimum value. Since collisions of excited mercury atoms with hydrogen molecules are known to be practically inelastic, the higher quantum efficiency for hydrazine cannot be due to difference in collision efficiency. It might very well be that collisions with hydrazine are much less efficient than with hydrogen, which would lead to longer reaction chains in the case of the former.

The rate of hydrazine decomposition was found to be forty times that for ammonia with excited mercury. A value of 13 molecules per quantum would, therefore, correspond to a quantum efficiency of 0.3 molecules for the sensitized ammonia decomposition. While not much confidence may be placed in this figure, it should be noted that Warburg[15] found the quantum yields for the photochemical decomposition to be 0.25 mol./$h\nu$ for light of wave length 2025–2140Å.

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[13] Taylor and Marshall, *J. Phys. Chem.*, 29, 1140 (1925).

[14] Marshall, *ibid.*, 30, 1078 (1926); Bates and Taylor, THIS JOURNAL, 49, 2446 (1927).

[15] Warburg, *Sitzb. preuss. Akad. Wiss.*, 746 (1911); 216 (1902).

Effect of Added Gases on the Rate.—A number of experiments were made in which nitrogen, hydrogen or ammonia was added initially to the hydrazine and the decomposition rate determined. The results are best illustrated by the curves of Fig. 5 and Fig. 6. The hydrazine pressures were from 9 to 11 mm. and the other gases were added in amounts up to 200 mm. In the experiments shown in Fig. 6 the rates were considerably reduced by increasing the distance of the arc and partially screening it with a copper gauze.

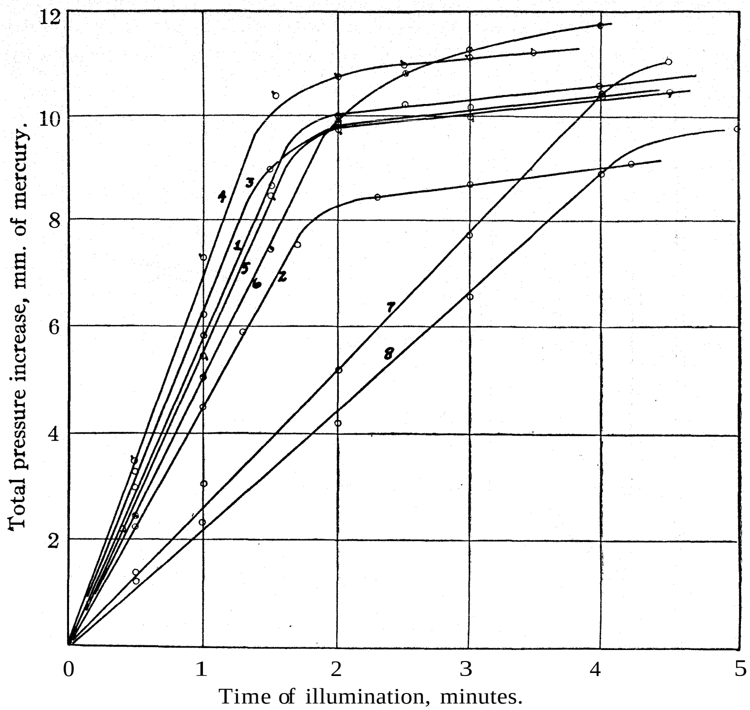

Fig. 5.—Effect of added gases on the rate of the photosensitized decomposition. Curves 1 and 2, hydrazine alone, pressures, 10.5 and 8.5 mm., respectively. Curve 3, hydrazine in presence of nitrogen, pressures, 10.0 and 200 mm., respectively. Curves 4 and 5, hydrazine with hydrogen present; pressure of hydrazine, 10.6 and 9.8 mm., respectively, pressures of hydrogen, 200 mm. and 25 mm., respectively. Curve 6, hydrazine with ammonia present; pressures. 10.8 and 175 mm., respectively. Curves 7 and 8, hydrazine with ammonia and hydrogen present; pressures of hydrazine approximately 10 mm., pressures of ammonia and hydrogen approximately 100 mm. each. Arc at a distance of 0.5 cm. for all these experiments.

Neither the presence of nitrogen, ammonia nor hydrogen exerts appreciable influence upon the rate of the sensitized decomposition; Slight variations in the slopes of the curves occur at random. They are undoubtedly to be attributed to experimental error in reading the time and pressure over small intervals and to slight variations in the arc intensity.

The failure of nitrogen or ammonia pressure to affect the rate is not surprising since their efficiency in quenching excited mercury is known to be very low.[16,17] The failure of hydrogen to affect the rate is, however, interesting. This result is in direct contrast to the sensitized ammonia decomposition which has been shown by Mitchell and Dickinson[17] to be strongly inhibited by small pressures of hydrogen. Practically every collision of excited mercury with hydrogen molecules results in its deactivation.[16] Hydrogen would, therefore, be expected to retard sensitized hydrazine decomposition. Indeed, with hydrogen pressures twenty times that of hydrazine, the retardation would be expected to be directly proportional to hydrogen pressure. The absence of any effect appears to be explicable only on the basis that the energy of those excited mercury atoms colliding with hydrogen molecules is still available for the decomposition of hydrazine.

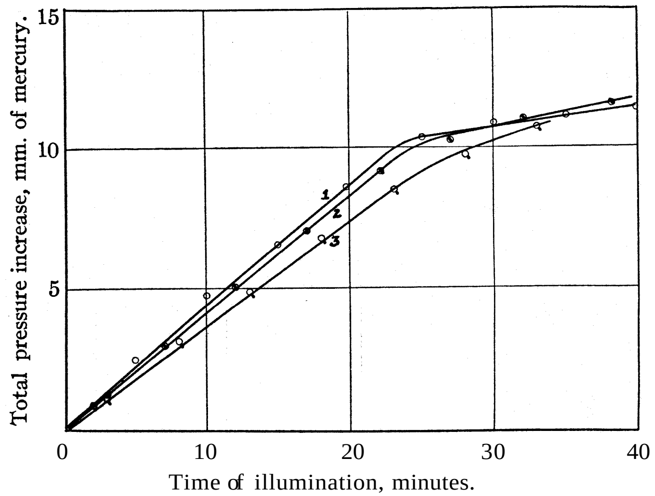

Fig. 6.—Effect of added gases on the rate of the photosensitized decomposition. Curve 1, hydrazine alone; pressure, 10.0 mm. Curve 2, hydrazine with hydrogen present; pressures, 10.0 mm. and 200 mm., respectively. Curve 3, hydrazine with ammonia and hydrogen present; pressures, 9.8 mm, 100 mm. and 100 mm., respectively. Arc at a distance of 6 cm. and screened in these experiments.

We may justifiably assume[18] that a collision of the second kind between

[16] Stuart, Z. *Physik*, **32,** 262 (1925).

[17] Mitchell and Dickinson, THIS JOURNAL, 49, 1478 (1927).

[18] See Taylor, *ibid.*, 48, 2840 (1926), for a partial summary of evidence.

a mercury atom in the 2^3P_1 state and a hydrogen molecule results in the dissociation of the latter

$$Hg' + H_2 \longrightarrow Hg + 2H$$

Hydrogen atoms must, therefore, react with hydrazine. It is our intention to test this conclusion by introducing hydrogen atoms into hydrazine.

Curves 7 and 8 in Fig. 5 for experiments in which mixtures of 100 mm. each of hydrogen and ammonia were admixed with hydrazine show a retardation of the rate, an effect produced by neither gas alone. It cannot, apparently, be attributed to experimental error. We are unable to offer a satisfactory explanation for it.

Effect of Light Intensity.—The reaction rates were considerably reduced by decreasing the light intensity materially and the latter varied by means of the previously described copper gauze screens. Care was taken to prevent variations in the intensity of the 2537 Å. line caused by variations in the running temperature and wattage of the arc. The results are summarized in Table V. Hydrazine pressures were constant to a few per cent. The galvanometer deflections given represent the average of two separate sets of determinations, the average of ten distinct deflections being taken to determine the true deflection for each different intensity. The experiment with no screen intervening was repeated between each of the others as a check. The rates given are the averages for twenty-minute periods taken during the experiment almost to the point of pressure doubling.

Table V

Effect of Incident Light Intensity on the Reaction Rate

	Rates		
	I No Screen	II Screen No 1	III Screen Nos. 1 and 2
Average Δp per 20 min.	2.40	0.91	0.33
Average Δp per 20 min.	2 00	.90	.35
Average Δp per 20 min.	2.20		
Average	2.20 (k_1)	.905 (k_2)	.34 (k_3)
	Relative Light Intensities		
Average galv. deflection	73.39 (l_1)	30.06 (l_2)	12.34 (l_3)
Ratios of reaction rates	$k_1/k_2 = 2.43$		$k_2/k_3 = 2.65$
Ratios of intensities	$l_1/l_2 = 2.44$		$l_2/l_3 = 2.44$

The results show that the velocity of hydrazine decomposition sensitized with mercury vapor is directly proportional to the incident light intensity.

The Absorption Spectrum of Gaseous Hydrazine

The results of studies of molecular spectra have led to the elucidation of the primary photochemical process in several systems involving diatomic molecules. Franck[19] has pointed out that according to the quantum theory

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[19] Franck, *Trans. Faraday Soc.*, 21, 536 (1925).

of light absorption the immediate result is the formation of an excited molecule, but that the excited molecule may then undergo spontaneous dissociation without the agency of collisions. This is the type of process occurring in the halogens, hydrogen halides and alkali halides. More complex molecules exhibit such complicated band spectra that detailed analysis has been impossible. It now appears quite certain that an entirely continuous molecular absorption spectrum corresponds to a primary dissociation of the molecules. One consisting of bands possessing a fine structure corresponds to a primary excitation of the molecule, which can then undergo dissociation only on collision, provided, of course, that the absorbed energy is comparable with that required for dissociation.

It was first pointed out by Henri[20] that certain molecules give a type of absorption spectrum consisting of diffuse or continuous bands. These bands are not resolvable into distinct lines even with very high dispersion and low pressures. According to Henri, such molecules as NH_3, H_2S, COS and CH_3NH_2 give this type of spectrum. His interpretation of this phenomenon is that the molecule upon light absorption goes into an electronically excited state, no longer quantized as to rotation, in which the molecule is strongly deformed in contrast to ordinary absorption processes. To such a state he gives the name "Predissociation." Bonhoeffer and Farkas[21] have discussed the ammonia spectrum in relation to predissociation, and have presented theoretical and experimental evidence for the assumption that the primary process is a separation of the ammonia molecule into parts, most probably NH_2 and H. They explain the diffuse bands upon the basis of such a process. Kronig[22] has apparently found justification for this idea from a theoretical viewpoint. From considerations based on wave mechanics he calculates that such a process is possible and also calculates the probability that it will occur. In the conclusion to their paper Bonhoeffer and Farkas state that according to the above idea the following cases of molecular decomposition processes must be distinguished. "First, the 'direct' or 'true photolytic processes' in which the molecule decomposes without the agency of outside collisions; secondly, the 'indirect,' in which the molecule is primarily excited and is then decomposed by collision with another molecule. The direct processes can be of various kinds. Either the molecule is primarily dissociated (I_2 in the continuum, HI), or the primarily excited molecule decomposes spontaneously without radiation (NH_3, predissociation spectrum)."

To obtain optical evidence for the primary process following light absorption by the hydrazine molecule we have investigated its absorption spectrum.

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[20] V. Henri, "Structure des Molécules," Librairie Scientifique J. Hermann, Paris, 1925.

[21] Bonhoeffer and Farkas, *Z. physik. Chem*, 134, 337 (1928).

[22] Kronig, *Z. Physik*, 50, 347 (1928).

Experimental

The continuous ultraviolet spectrum from a hydrogen discharge tube served as a light source for the absorption study. The discharge tube was the water-cooled type first described by Bay and Steiner.[23] It was constructed before their later modifications were published. The tube was run on approximately 10,000 volts and a current of 0.35 to 0 4 ampere. Hydrogen pressures of 8–10 mm. were employed. A side reservoir was attached in such a manner that the addition of hydrogen was simplified. As operated the tube provided a very intense source of continuous ultraviolet light extending to a region somewhat below 2000 Å. One to two minutes were sufficient for an intense exposure with a very narrow slit and the spectrograph at a distance of half a meter. Exposures of five minutes were required at a meter distance. When desired the tube could be operated continuously for several hours. Its spectrum contained several emission lines on the continuous background in the visible and near ultraviolet. No attempt was made to identify or remove them as they were beyond the region in which hydrazine absorbs.

A Type E-2 Hilger quartz spectrograph- giving an average dispersion of 6 Å. per millimeter between $\lambda = 2492$ Å. and X = 2293 A. and 5 Å. per millimeter from $\lambda = 2276$ Å to $\lambda = 2199$ Å. was employed. The spectrum of the copper arc served for reference. The vapor from a sample of the hydrazine used in the photochemical experiments was employed, the absorption tube being refilled before each exposure. Absorption tubes 20 and 80 cm. in length and pressures from several tenths up to ten mm. were used

Results

The spectrograms obtained show that gaseous hydrazine absorbs measurably in the ultraviolet below about 2490 Å. Absorption becomes appreciable below 2440 Å. The spectrum consists of a series of faint diffuse bands which appear to become wider and more diffuse toward shorter wave lengths. Apparently continuous absorption then sets in and becomes stronger toward the ultraviolet. With an absorbing thickness of 80 cm. and a pressure of 0.5 mm. the band absorption commences at about 2490 Å., continuous absorption beginning at about 2370 Å. It was not possible to produce absorption of longer wave lengths by increasing the pressure to 10 mm. With the absorbing thickness reduced to 20 cm. and at about 1 mm. pressure, faint indications of the bands are visible down to 2260 Å. Below, a region of apparently continuous absorption extends. Lowering of the pressure to a few tenths of a millimeter did not extend the beginning of the continuum further toward shorter wave lengths. On account of their faintness the bands are scarcely visible on a reproduction of the spectrograms.

There appear to be six or seven separate diffuse bands between 2490 and 2260 Å., separated by equal intervals of about 3 or 4 Å. Those from 2490 to 2370 Å. are more sharply defined. The bands range in width from 8 Å. to approximately 25 Å. toward the ultraviolet. The limits, however, cannot be indicated with precision. They appear to be absolutely continuous and resemble closely those obtained by Henri[20] with methylamine in the

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[23] Bay and Steiner, Z. *Physik,* **45, 337** (1927); **Z. *Elektrochem* , 34,** 660 **(1928).**

region from 2362 to 2288 Å. and the bands of ammonia, which occur from 2260 to 1600 Å.,[24] although separated by considerably smaller intervals than in these cases. Conclusive evidence as to whether the bands of the hydrazine absorption spectrum may be resolved into fine lines will have to be obtained with an instrument giving higher dispersion. This was not available during the performance of these experiments. It appears for the present, however, that in hydrazine we have also a case of "predissociation."

Discussion

Hydrazine Decomposition.—While the results of the purely photochemical study may be regarded as only qualitative, those obtained in the sensitized decomposition provide quantitative information from which a reaction mechanism may be obtained. The experimental observations for which a theory of the reaction mechanism must account are, briefly: (1) the nature of the products, (2) speed of reaction and chain mechanism and *(3)* the absence of retardation by hydrogen, which is most easily understandable on the basis that atomic hydrogen reacts with hydrazine.

For the primary process following reception of energy by the hydrazine molecule on a collision of the second kind with excited mercury or by absorption of a light quantum, we need consider only two possibilities. The formation of an activated hydrazine molecule may take place, reaction then occurring only on collision with a normal molecule. Alternatively, the primarily excited molecule may split directly into parts which then undergo reaction with normal molecules.

The mechanism based on the first possibility would be

$$N_2H_4 + Hg' \longrightarrow N_2H_4' + Hg$$
$$N_2H_4' + N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$$

This leads to a value of two molecules as the maximum possible quantum efficiency. It does not agree with the observed minimum quantum efficiency of 13 molecules or the chain mechanism, nor will it account satisfactorily for the failure of hydrogen to retard the rate.

Formulation of a mechanism based on the second possibility leads to more satisfactory results. Four possible ways in which the primarily excited molecule may split must be considered. These are

$$N_2H_4 + Hg' \longrightarrow N_2H_4' + Hg$$
$$\text{(a)}\quad N_2H_4' \longrightarrow N_2H_3 + H$$
$$\text{(b)}\quad N_2H_4' \longrightarrow 2NH_2$$
$$\text{(c)}\quad N_2H_4' \longrightarrow N_2H_2 + H_2$$
$$\text{(d)}\quad N_2H_4' \longrightarrow NH_3 + NH$$

On the basis of the most recently accepted value of 9.5 volts,[25] or 219,000 calories, for the heat of dissociation of the nitrogen molecule, breakage of

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[24] Leifson, *Astrophys. J.*, 63, 73 (1926).

[25] Mulliken, *Phys. Review*, 32, 761 (1928).

a N–H bond requires 90,000 calories of energy. The energy available from an excited mercury atom is 112,000 calories, so that (a) is possible from the standpoint of energetics. The heat of formation of anhydrous hydrazine has not been measured, nor are data for the energy of an N–N bond in such a case available. It is, therefore, impossible to calculate with certainty whether the quantum of absorbed energy is sufficient for the other three processes. Some idea as to the energy required ruay be obtained in the following manner. The reaction $N_2 + 2H_2 + \text{aq} \longrightarrow N_2H_4$ (dissolved) is endothermic by 9500 calories.[26] In solution hydrazine exists as the hydrate. There is justification for the belief that the heats of solution and of hydration are positive, which leads to the conclusion that the formation of anhydrous hydrazine from the elements is endothermic by an amount greater than, say, 10,000 calories. If we take this value for the heat of formation of hydrazine, 90,000 calories as the heat of formation of an N–H bond and values of 101,000 calories for the heat of dissociation of hydrogen and 219,000 calories for that of nitrogen, we may calculate that Process (b) requires 49,000 calories and (d) 49,000 calories. On the assumption that the energy required is that for breaking two N–H bonds independently, minus the heat of combination of two hydrogen atoms, we obtain for Process (c) a value of 80,000 calories. All four types would then be possible with the quantum of 112,000 calories. It is uncertain as to how much confidence may be placed in the results of such calculations.

The sequence of secondary reactions which must follow in case (c)

$$N_2H_2 + N_2H_4 \longrightarrow 2NH_3 + N_2$$

and in case (d)

$$NH + N_2H_4 \longrightarrow NH_3 + N_2 + H_2$$

while accounting for the products, eliminate these as possible mechanisms. They will not account for the observed chain mechanism or for non-retardation by hydrogen. It has been found[27] that hydrazine is formed when ammonia is passed through a cooled high tension arc. The authors state that the most probable explanation lies in a decomposition of the ammonia into NH and H_2 by electron impact, and formation of hydrazine by the reaction

$$NH + NH_3 \longrightarrow N_2H_4$$

In this case ammonia should retard the rate if the mechanism were according to (d). This is contrary to experimental fact.

Assumption of either (a) or (b) as the primary process leads to a mechanism better in accord with our experimental observations. Thus

$$N_2H_4 + Hg' \longrightarrow N_2H_4' + Hg \longrightarrow N_2H_3 + H + Hg \qquad (1)$$
$$N_2H_3 + N_2H_4 \longrightarrow 2NH_3 + N_2 + H \qquad (2)$$
$$H + N_2H_4 \longrightarrow N_2H_3 + H_2 \qquad (3)$$

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[26] *Berthelot and Matignon, Compt. rend., 113,* **672 (1891).**

[27] **G.** *Bredig and A.* Koenig, *Naturwissenschaften,* **24,493 (1928).**

Reactions such as

$$\left.\begin{array}{r} H + H \longrightarrow H_2 \\ N_2H_3 + H \longrightarrow N_2H_4 \end{array}\right\}\text{ wall reaction} \qquad \begin{array}{r}(4)\\(5)\end{array}$$

woud lead to breaking of the reaction chains. With (b) the mechanism would be

$$\begin{array}{rl} N_2H_4 + Hg' \longrightarrow N_2H_4' + Hg \longrightarrow 2NH_2 + Hg & (1) \\ NH_2 + N_2H_4 \longrightarrow NH_3 + N_2 + H_2 + H & (2) \\ H + N_2H_4 \longrightarrow NH_2 + NH_3 & (3) \end{array}$$

The reactions

$$\left.\begin{array}{r} H + H \longrightarrow H_2 \\ NH_2 + NH_2 \longrightarrow N_2H_4 \end{array}\right\}\text{ wall reaction} \qquad \begin{array}{r}(4)\\(5)\end{array}$$

break the reaction chains. The reaction, $NH_2 + H_2 \longrightarrow NH3 + H$, which may be suggested, is endothermic by about 11,000 cal. and probably does not play a material role at room temperatures. Either of the above mechanisms satisfactorily accounts for the observed facts.

Either of the above mechanisms, on the assumption that reactions such as (4) and *(5)* limit the reaction chains, requires a proportionality of the reaction rate to incident light intensity involving the square root of the latter.[28] In the present instance the rate is directly proportional to the incident intensity. This is reconciled with the postulated mechanisms if we assume that Reactions 4 and 5 take place on the walls of the containing vessel, the rate of disappearance then being unimolecular with respect to the concentrations. It is probable that such reactions never take place except on the walls of the containing vessel. Similar disagreement exists for other photochemical reactions and is thus explained.

The evidence at present available offers no basis upon which to decide which of the preceding mechanisms is the more probable. It may be of interest to record the thermal values for the various secondary reactions given, calculated from the previously assumed thermal date.

$$\begin{array}{r} H + N_2H_4 \longrightarrow N_2H_3 + H + 11{,}000\text{ cal.} \\ H + N_2H_4 \longrightarrow NH_2 + NH_3 + 40{,}000\text{ cal.} \\ N_2H_3 + N_2H_4 \longrightarrow 2NH_3 + N_2 + H + 28{,}000\text{ cal.} \\ NH_2 + N_2H_4 \longrightarrow NH_3 + N_2 + H_2 + H - 1000\text{ cal.} \end{array}$$

While the mechanisms formulated are based on the results of the investigation of the sensitized decomposition, there is no reason to believe that the purely photochemical decomposition proceeds by another mechanism,

The spectral evidence offered by the hydrazine absorption spectrum is not entirely conclusive. It is, however, in accord with our suggested mechanism if we accept the Bonhoeffer and Parkas conclusion[21] concerning the process giving rise to a spectrum consisting of continuous bands. Indeed, we may state that if it can be conclusively shown that the hydra-

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[28] Kistiakowsky, "Photochemical Processes," The Chemical Catalog Company, Inc., New York, 1928, p. 96.

zine bands do not possess a fine structure our results provide strong evidence in support of this idea concerning the Henri "predissociation spectra." A study of the photochemical decomposition of methylamine, which has been definitely shown by Henri to possess a spectrum of this type, should prove of interest in this connection, Such a study is to be undertaken.

This investigation was carried out during the tenure, by one of us (J.C.E.), of a du Pont Fellowship at Princeton University. We take this opportunity of expressing to the E. I. du Pont de Nemours Company of Wilmington, Delaware, our sincere appreciation of this assistance.

Summary

Gaseous hydrazine is decomposed photochemically by the ultraviolet radiation from a quartz mercury arc. A more rapid decomposition is brought about by optically excited mercury atoms. The products of the reaction in both cases are ammonia, nitrogen and hydrogen in amounts indicating a reaction according to the stoichiometric equation $2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$. Decomposition of the ammonia formed follows this reaction.

The products from the thermal decomposition in a quartz bulb indicate reaction mainly according to the equation $3N_2H_4 \longrightarrow 4NH_3 + N_2$. The reaction is heterogeneous and unimolecular in character.

The rate of the purely photochemical decomposition is uninfluenced by temperature or by the presence of large concentrations of ammonia or hydrogen. The photochemical decomposition of ammonia proceeds at a rate one-tenth that of hydrazine under the same conditions.

The sensitized hydrazine decomposition is a very rapid reaction. Its rate is forty times that of ammonia under identical conditions. Hydrazine decomposition is a chain reaction. A minimum quantum efficiency of 13 molecules per absorbed quantum has been found for it. The rate of the sensitized reaction is unaffected by the presence of nitrogen, ammonia or hydrogen in large concentrations. The lack of retardation by hydrogen is explained on the basis that hydrogen atoms react with hydrazine. The rate of the sensitized decomposition is directly proportional to the incident light intensity.

The absorption spectrum of gaseous hydrazine has been investigated. Hydrazine vapor absorbs appreciably in the ultraviolet below 2440 Å. The spectrum consists of a series of faint, apparently continuous bands, followed by a region of continuous absorption. The limits of the regions of absorption depend upon the density of the absorbing layer. With the dispersion employed it cannot be stated conclusively that the absorption bands do not possess a fine structure. It appears for the present that hydrazine presents a case of "predissociation."

The results obtained are satisfactorily explained by a reaction mechanism based upon a dissociation of the primarily excited molecule as a primary process and not one involving an activated molecule. Agreement is obtained if the dissociation is either into N_2H_3 and H or $2NH_2$. Thermal calculations for the various primary and secondary processes discussed are given. The nature of the absorption spectrum is in accord with such a mechanism if the idea of Bonhoeffer and Farkas be accepted.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SOLUBILITY OF CALCIUM CARBONATE (CALCITE) IN CERTAIN AQUEOUS SOLUTIONS AT 25°[1]

BY G. L. FREAR[2] AND JOHN JOHNSTON

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The solubility of calcium carbonate in aqueous solutions, as influenced by the partial pressure of carbon dioxide in the system and by the presence of other salts, is of interest because of its significance in relation to the problem of scale formation in steam boilers and pipes, to the study of bone calcification and of blood equilibria in physiological systems, and to a better understanding of the process of deposition of carbonates under geological conditions. The work to be presented comprises precise determinations of the solubility of calcite at 25° in the presence of carbon dioxide at pressures varying from 0.0003 to 1.0 atmosphere, in water and in a series of solutions of sodium chloride and of calcium sulfate, including solutions saturated also with respect to gypsum ($CaSO_4 \cdot 2H_2O$).

The papers on the solubility of calcium carbonate in water, prior to 1915, have been reviewed in an earlier paper;[3] since that time a number of other contributions have been published.[4] A plot of all of the data,

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[1] From the dissertation presented by G. L. Frear to the Graduate School of Yale University, June, 1926, in candidacy for the degree of Doctor of Philosophy.

[2] Loomis Fellow, 1925–1926; Sterling Fellow, 1926–1927.

[3] Johnston, THIS JOURNAL, 37, 2001 (1915).

[4] (a) Cavazzi, *Gazz. chim. ital.*, II 46, 122 (1916); solubility of $CaCO_3$ in water at 0–15° and 1 atm. of CO_2; (b) Bäckström, *Z. physik Chem*, 97, 179 (1921), solubility of calcite and aragonite at 9, 25 and 35° and approximately 1 atm. of CO_2; see also Bäckstrom, THIS JOURNAL, 47, 2432, 2443 (1925); (c) Mitchell, *J. Chem. Soc.*, 123, 1887 (1923), solubility of calcite, and of calcite with nesquehonite ($MgCO_3 \cdot 3H_2O$), at 25° and 4–24 atm. of CO_2; (d) Haehnel, *J. prakt. Chem.*, 107, 165 (1924), solubility of $CaCO_3$ in water at 18° and 10–56 atm. of CO_2, and up to 50° at 56 atm.; (e) Hastings, Murray and Sendroy, *J. Biol. Chem.*, 71, 723 (1927), solubility of $CaCO_3$ at 38° in some solutions of NaCl and in serum; (f) with respect to the three crystal forms of $CaCO_3$, see Johnston, Merwin and Williamson, *Am. J. Sci.*, 41, 473 (1916); Gibson, Wyckoff and Merwin, *Am. J. Sci.*, 10, 325 (1925); (g) W. D. Kline, "Dissertation," Yale University, 1923.

including Kline's results (presented later, in Table 111), leads to the following values.[5]

TABLE I

THE SOLUBILITY OF CALCITE AT 25°

CO_2, partial pressure, atm.	0.00032	0.001	0.01	0.1	1.0	10
$CaCO_3$, millimoles per kilo water	0.53	0.78	1.7	3.9	9.0	22.5

The temperature coefficient of the solubility is, within the accuracy of the measurements, independent of the partial pressure of carbon dioxide, particularly in the range 0.0003–1 atm.; consequently it suffices to give the ratio r of the solubility at $t°$ to that at 25°.

TABLE II

THE RATIO (r) OF THE SOLUBILITY AT $t°$ TO THAT AT 25°

t	0°	10°	20°	25°	30°	50°
r	1.8	1.4	1.1	1.0	0.9	0.6

These values of r are on the line $\log r = 830/T - 2.78$; this formula, when extrapolated to 100°, yields results in harmony with analyses of waters from boilers.

In presenting our results we shall adopt a notation made use of in a previous paper,[6] dealing with equilibrium in solutions of alkali carbonates in terms of activities. The activity of carbonic acid (H_2CO_3)[7] may be written

$$(H_2CO_3) = \gamma\lambda cP \qquad (1)$$

where P is the partial pressure, in atmospheres, of carbon dioxide in the gas phase in equilibrium with the solution; c is the total molal concentration of carbon dioxide in the solution when P is unity and γ and λ are the activity coefficients of H_2CO_3 and of water, respectively. We also write

$$(H^+)(HCO_3^-)/(H_2CO_3) = K_1$$
$$(H^+)(CO_3^=)/(HCO_3^-) = K_2$$
$$(Ca^{++})(CO_3^=) = K_C$$

K_C being the activity product constant for calcium carbonate (calcite); whence by combination with (1)

$$(Ca^{++})(HCO_3^-)^2/P = \gamma\lambda cK_CK_1/K_2 \qquad (2)$$

If α_1 and α_2 denote the activity coefficients of Ca^{++} and HCO_3^-, respectively, and m_1 and m_2 the corresponding molalities, Equation 2 may be written

$$P/m_1m_2^2 = \alpha_1\alpha_2^2(K_2/(K_1K_C\gamma\lambda c)) = f'(m) \qquad (3a)$$

Determinations, in a series of equilibrated solutions, of the quantities P, m_1 and m_2 enable one to calculate directly the corresponding value of the function f'(m). Equation 3a may be more conveniently expressed

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[5] With respect to the solubility at smaller pressure, see Johnston and Williamson, THIS JOURNAL, 38,975 (1916).

[6] Walker, Bray and Johnston, *ibid.*, 49,1235 (1927).

[7] Parentheses denote an activity; brackets, a concentration.

in terms of the mean molality m and the mean activity coefficient α of $Ca(HCO_3)_2$. By definition $m = \sqrt[3]{m_1m_2^2}$ and $\alpha = \sqrt[3]{\alpha_1\alpha_2^2}$. It follows that

$$P^{1/3}/m = \alpha\sqrt[3]{K_2/(K_1K_C\gamma\lambda c)} = f(m) \tag{3}$$

The function $f(m)$ contains a factor K_2/K_1K_C independent of concentration; as m and P approach zero, α_1 and α_2 by definition approach unity; when $m_1 = 0$, c_0 is the solubility of carbon dioxide in water and we have $c_0\gamma_0\lambda_0 = c\gamma\lambda$. Thus by plotting $f(m)$, evaluated directly from the experimental results, against the concentration, we are enabled to estimate $f(0)$, the value of $f(m)$ obtained by extrapolation to zero concentration of salt and, since $(\alpha_1\alpha_2^2)_m/(\alpha_1\alpha_2^2)_0 = f(m)/f(0)$, by substitution of the appropriate values of the other factors, to calculate, from the intercept $f(0)$, the actual solubility product of calcite applicable at any pressure within the range of solutions investigated if the assumption is made that $(\alpha_2)_0$ is equal to unity, which probably is not seriously in error and is the best approximation than can be made at the present time. In this connection it is important to note that at very small pressures of CO_2, probably of the order of 10^{-14} atm.,[5] the relative amount of Ca^{++} associated with OH^- so far exceeds that present in solution as carbonate and bicarbonate that $Ca(OH)_2$ becomes the stable solid phase in place of $CaCO_3$; thus f(0) is merely a virtual quantity, but this fact does not diminish its significance or interfere with the process of extrapolation.

If, besides calcite, gypsum is in equilibrium with the solution, the additional solid phase imposes the further condition defining the solubility product of gypsum K_G, *i*. e.,

$$(Ca^{++})(SO_4^{=}) = K_G$$

By combination of this condition with relations similar to those developed above, and correcting for incomplete ionization, Stieglitz[8] calculated the saturating concentration of calcium carbonate and of calcium sulfate in sea water as functions of the partial pressure of CO_2 in the atmosphere. Provided that no change in the nature of the solid phases occurs, the equality of the ratios must be valid

$$(CO_3^{=})/(SO_4^{=}) = K_C/K_G \tag{4}$$

However, there is some mineralogical evidence of the possibility of reaction between $CaSO_4$ and $CaCO_3$ (possibly as aragonite) under appropriate conditions with the formation of a solid solution or a double salt, in which event deviations from Equation 4 are to be expected. Thus Doss[9] found that certain fresh water limestones and tuffs contain appre-

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[8] J. Stieglitz, "The Relation of Equilibrium between the Carbon Dioxide of the Atmosphere and the Calcium Sulfate, Calcium Carbonate, and Calcium Bicarbonate in Water Solutions in Contact with It" in "The Tidal and Other Problems" by T. C. Cliamberlin, *et* al. Carnegie Inst. Publ. No. 107 (1909).

[9] B. Doss, "Neues Jahrbuch für Mineralogie und Geologie," 1897, Vol. I, p. 105.

ciable quantities of sulfate and of water in proportions approximately equal to their ratio in pure gypsum; the inclusions visible at 2000 diameters' magnification accounted for not more than one-twentieth of the sulfate present. Vater[10] prepared calcite crystals in gypsum solutions and observed that they possessed a high sulfate content which he thought could not be attributed to inclusions of the mother liquor or to ingrown crystals of gypsum.

Little information for the solution of this problem is to be obtained from the results of Shipley and McHaffie[11] in their attempt to investigate, by means of electrometric titration, the influence of calcium sulfate on the hydrogen-ion concentration of carbonate solutions; failure to recognize the interdependence of the equilibria involved in this system led these authors to the unwarranted conclusions that the ionization constants of carbonic acid vary and that alkaline earth bicarbonates do not exist in aqueous solutions.

In unsaturated solutions of $CaSO_4$, the solubility of $CaCO_3$ depends upon the common ion effect and upon the influence of the total ion concentration on the activities of the chemical species involved in the equilibrium. Solubility determinations in solutions of hetero-ionic salts are of interest for the study of the influence of ionic strength on these activities, At best the data of Cameron and his co-workers[12] and of Seyler and Lloyd[13] are of merely qualitative significance as experimental conditions were insufficiently controlled.

The Solubility of Calcite in Water at 25°.[14]—Mixtures of air and carbon dioxide in fixed proportions[15] were passed through reaction flasks, of the type used for the equilibration of solutions of alkali carbonates,[6] containing calcite crystals in contact with conductivity water. After equilibrium had been attained, the partial pressure of carbon dioxide and the total molality of base in solution[16] were determined; the mean results are assembled in the first two columns of Table III. The third column gives the bicarbonate molality $[HCO_3^-]$; the fourth, the ionic strength $\mu = (2[Ca^{++}] + 2[CO_3^{--}] + \frac{1}{2}[HCO_3^-])$; and the last, the function $f(m) = P^{1/3}/m$. The bicarbonate molality was arrived at by deducting from the calcium molality $[Ca^{++}]$ an amount equivalent to the carbonate molality $[CO_3^{--}]$, that of hydroxyl $[OH^-]$ being negligible at the partial pressure of carbon dioxide in these experiments. The correction, which in no case exceeds 2%, may be estimated with sufficient accuracy by introducing into Equation 3 the extrapolated value of $\gamma\lambda c K_1/K_2$ (which is 310)[6] and the activity coeffi-

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[10] Vater, *Z. Krist.*, 21, 460 (1893).

[11] Shipley and McHaffie, J. *Soc.* Chem. *Ind.*, **42,** 310T, 321T (1923).

[12] Cameron, Bell and Robinson, **J.** Phys. *Chem.*, 11, 414 (1907); Cameron and Robinson, *ibid.*, 11,577 (1907).

[13] Seyler and Lloyd, J. Chem. *Soc.*, 95, 1347 (1909).

[14] Experimental work by Dr. W. D. Kline.

[15] For the method of preparation and analysis of such mixtures, see Johnston and Walker, THIS JOURNAL, 47,1807 (1925).

[16] See Johnston, *ibid.*, 38, 947 (1916); Walker, Bray and Johnston, *ibid.*, 49, 1235 (1927).

cient of $MgSO_4$ and of $Ba(IO_3)_2$[17] as approximations to that of $CaCO_3$ and $Ca(HCO_3)_2$ at corresponding ionic strengths; when P exceeds 0.01, the correction is less than the experimental uncertainty in the determination of total base, and so may be neglected. The results so calculated are, we venture to believe, more reliable than any hitherto available.

TABLE III

EXPERIMENTAL REDETERMINATIONS (BY W. D. KLINE) OF THE SOLUBILITY OF CALCITE IN WATER AT 25°

Partial press. of CO_2, atm, P	Calcium mol, mml / kilo H_2O, 1000 $[Ca^{++}]$	Bicarb. mol, mml./ kilo, H_2O, 1000 $[HCO_3^-]$	Ionic strength μ	Log $f(m)$ = log $P^{1/3}/m$
0.00031	0.52	1.02	0.00157	1.9194
.00038	0.56	1.10	.00169	1.9162
.00093	0.76	1.50	.00229	1.9119
.00334	1.17	2.32	.00352	1.9082
.00690	1.51	3.01	.00454	1.9009
.0160	2.01	4.01	.00603	1.8983
.0432	2.87	5.74	.00861	1.8866
.1116	4.03	8.06	.01209	1.8766
.9684	8.91	17.82	.02673	1.8448

The Solubility of Calcite in Aqueous Solutions of Calcium Sulfate and of Sodium Chloride.—Calcite for the following experiments was prepared by adding dropwise with constant stirring a solution of ammonium bicarbonate to a purified solution of calcium chloride; after the precipitation had been completed, ammonium chloride was added and the mixture was stirred continuously for several hours at 80°. The product after thorough washing was heated in a Rose crucible in a stream of carbon dioxide to remove any remaining traces of ammonium salts. Examination with a petrographic microscope showed crystals of calcite ranging in average dimensions from 0.01 to 0.1 mm

Natural gypsum, the analysis of which indicated a high purity, was split into small blocks, the fine particles being removed by screening. Sodium chloride was recrystallized from commercial "c. p." stock.

In all of the experiments conducted at roughly one atmosphere of carbon dioxide the procedure employed was very similar to that outlined in the preceding section. In the earlier experiments with lower partial pressures of carbon dioxide, equilibrium was established by causing a motor-driven circulating pump, consisting of mercury valves with a mercury column as piston, to pass a mixture of air and carbon dioxide continuously around a closed glass system consisting of a one-liter pyrex glass reaction flask in series with a group of gas-sampling pipets in parallel with one another. In order to avoid rubber connections, the various parts of the system were joined to one another through mercury seals. The reaction flask was clamped in an air thermostat maintained at a temperature of 25 ± 0.05°. The approach to equilibrium was observed by analyzing the gas phase at intervals; ordinarily a week was allowed for the system to attain equilibrium.

As the circulating system just described did not establish equilibrium so rapidly as had been anticipated, and as the arrangement for sampling was not quite satisfactory, a different form of apparatus (Fig. 1) was devised and used in the later work. The

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[17] As given by Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 344, 375.

purpose of this device is to cause the solution to pass repeatedly back and forth through a filter containing the solid phase so that the movement of the liquid provides the pump action for circulating the gas. The two 200-cc. bulbs (A, A') are joined to a short neck B into each end of which is sealed a perforated glass plate to serve as a partition preventing any of the solid phase from passing into either bulb. Midway between the plates the neck is provided with a wide glass-stoppered side-tube for introducing the crystals of the saturating solute and, if necessary, the wads of cotton to act as filters.[18] Sealed through the ends of the bulbs, Tubes D and D′ are connected by ground-glass joints with the opposite ends of Pipet C, which is provided with suitable stopcocks for isolating a sample of the gas phase. A cam, driven by an electric motor through a train of speed reducers and connected to the equilibrium apparatus through suitable gearing, causes the apparatus to turn from an initially vertical position through a half revolution, to remain upright long enough to allow most of the solution to filter from one bulb to the other and then to return to its original position, where there is another pause before the cycle is repeated. Intermittent oscillation is employed in preference to interrupted rotation as it permits the apparatus to be mounted so that the cylindrical axis of the pipet never occupies a lower level than the solution in the bulbs; thus the danger of blocking the passage of the gas to and through the pipet with solution is avoided. The gas displaced from the lower bulb by the inflowing solution forces an equal volume to bubble from the pipet into the solution in the upper bulb through the upturned tips of Tubes D, D′. This combination of filtration and bubbling affords ample contact of the liquid with the solid and the gas phases without danger of pulverizing the crystals. Trial experiments with calcite at various partial pressures of carbon dioxide indicated that equilibrium conditions are attained in two to three days when the volume of the solution is 100 cc., the weight of calcite is 2 g. and filtration is in progress four minutes of the five in each cycle. The apparatus may be conveniently mounted in a water thermostat. At the end of a run the motion is stopped so as to allow the solution to run completely into the bulb A', the stopcocks on the pipet are closed and the apparatus is removed bodily from the thermostat. The pipet is then disconnected at the ground joints and samples of the equilibrium solution are allowed to run through Stopcock E into tared glass-stoppered flasks containing known weights of standard hydrochloric acid. The stopcock, E, permits regulation of the sample size so as to bring the contents of the titration flasks nearly to the end-point. Owing to the strong tendency of calcium bicarbonate solutions to remain supersaturated when not in contact with solid $CaCO_3$, there is little opportunity for the solution to change in concentration while the samples are being withdrawn.

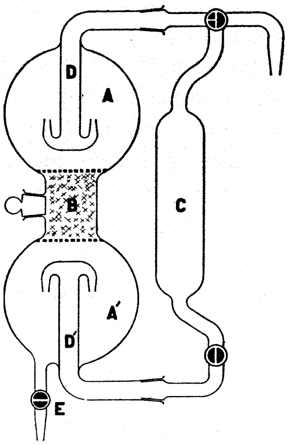

Fig. 1.—Equilibration apparatus.

The data in Table IV were obtained from runs of three or four days' duration. The partial pressure of carbon dioxide in the gas phase was determined by measuring the volume of gas before and after absorption in potassium hydroxide solution; from the known capacity of the pipet

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[18] When the crystals of the saturating solute are sufficiently large, the cotton may be dispensed with so as to avoid delay in the attainment to equilibrium from absorption effects.

the partial pressure of carbon dioxide could then be computed. The total base content of the solution was then determined in duplicate samples by the customary method except that care was taken to saturate the titrated solution with carbon dioxide gas immediately prior to the addition of the final few drops of standard reagent, the purpose of this precaution being to avoid difficulty in case the carbon dioxide liberated in the titration should be insufficient completely to saturate the mixture. For the determination of sulfate concentrations, precipitation as barium sulfate according to the directions of Johnston and Adams[19] was employed. Sodium chloride concentrations were determined by analysis for chloride either gravimetrically or volumetrically with ammonium thiocyanate and silver nitrate.

The results of the experiments on the solubility of calcite in saturated and in unsaturated calcium sulfate solutions are given in Table IV, which does not include the less precise results secured by means of the mercury circulating pump method except at partial pressures of carbon dioxide under which no corresponding measurements by the improved method were made. The first three columns list the mean experimental determinations of the partial pressure of carbon dioxide in atmospheres and the coexisting molalities of calcium bicarbonate and of calcium sulfate, re-

TABLE IV

ANALYSES OF SOLUTIONS SATURATED WITH BOTH CALCITE AND GYPSUM AT 25°

Partial press., of CO_2, atm., P	Bicarb. mol. mml./kilo H_2O $1000[Ca(HCO_3)_2]$	Sulfate mol. mml./kilo H_2O $1000[CaSO_4]$	μ	Log $f(m)$
0.121[a]	3.11	14.43	0.0671	1.750
.167[a]	3.56	14.24	.0676	1.756
.270	4.34	13.99	.0690	1.764
.431	5.31	13.48	.0698	1.770
.598	6.22	13.25	.0717	1.766
.652	6.42	13.27	.0723	1.768
.728[a]	6.71	13.41	.0738	1.767
.770[a]	6.95	13.46	.0747	1.764
.897[a]	7.40	13.60	.0766	1.763
.916[a]	7.53	13.41	.0762	1.762
.957	7.51	13.20	.0753	1.770
.963	7.55	13.20	.0754	1.769
.960	7.55	12.98	.0748	1.771
.953	7.58	13.17	.0754	1.767
.966	7.85	8.51[b]	.0576	1.793
.962	8.30	4.13[b]	.0414	1.816

[a] By mercury circulating pump method. The uncertainty in these measurements proves to be in the sulfate rather than in the carbonate concentration; the reason for this is not clear.

[b] Not saturated with respect to gypsum.

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[19] Johnston and Adams, THIS JOURNAL, 33, 829 (1911).

spectively; the fourth column gives the ionic strength; and the last column contains the values of log $f(m)$ where, as before, $f(m) = P^{1/3}/m$, both experimentally determined.

In Table V are brought together, likewise, the best results of the solubility determinations on calcite in sodium chloride solutions. In most of these experiments the method used was to bubble a stream of carbon dioxide through the salt solution in contact with calcite crystals; the oscillating equilibration apparatus, which was developed later, was employed in the single experiment indicated by the asterisk. A number of results for more concentrated salt solutions than are shown in Table V have not been included because, apparently, complete equilibrium was not attained in spite of the fact that a period of a week was allowed before the final sample was taken. This slowness was especially noticeable in the more concentrated salt solutions, and consequently these results are less concordant. The experimental procedure offers less likelihood of supersaturation than of incomplete saturation, so that the points indicating higher solubility are apparently the more reliable; the single result obtained with the improved form of apparatus is in conformity with this view. The work of Cameron Bell and Robinson[12] indicates a higher solubility than we have observed; their method, however, offers some possibility of supersaturation and their solid phase may not have been pure calcite which, being the most stable, is the least soluble of the three forms of calcium carbonate.

TABLE V

SOLUBILITY OF CALCITE IN SODIUM CHLORIDE SOLUTIONS AT 25°

Partial press. of CO_2, atm., P	Bicarb. mol. mml/kilo H_2O 1000[$Ca(HCO_3)_2$]	Chloride mol mml/kilo H_2O 1000[NaCl]	μ	Log f(m)
0.965	8.96	3.79	0.0307	1.842
.965	9.37	14.8	.0429	1.822
.965	9.67	34.8	.0638	1.809
.962	10.70	82.8	.115	1.764
.958	12.41	236	.273	1.699
.963	12.34	297	.334	1.703
.953	14.73	599	.643	1.624
.968	14.67	816	.860	1.628
.955*	15.55	878	.925	1.601
.953	14.55	1089	1.133	1.630
.968	16.18	1154	1.203	1.585

Discussion of Results

The last column of Table III shows again that the concentration of calcium bicarbonate in solution varies roughly as the cube root of the partial pressure of carbon dioxide through the range investigated. Indeed a plot of [$Ca(HCO_3)_2$] against $P^{1/3}$ is the most convenient method of interpolating to ascertain the solubility of calcite at any pressure of carbon dioxide, the graph being nearly linear. When this is done for the data in Table III and IV, we obtain the results listed in Table VI; it also gives, in the fifth column, the saturation concentration [$CaSO_4$] which diminishes as P, and hence [$Ca(HCO_3)_2$] increases.

TABLE VI

COMPARISON OF SOLUBILITY OF CALCITE IN WATER AND IN SOLUTIONS SATURATED ALSO WITH GYPSUM, AT A SERIES OF VALUES OF *P*

		Solubility (millimoles per kilo) of			
		Calcite in		$CaSO_4$ in	
$P^{1/3}$	P	H_2O s	$H_2O-CaSO_4$ s'	$H_2O-CaCO_3$ s''	$s's''/s$
0.5	0.125	4.21	3.16	14.35	10.8
.6	.216	5.13	3.97	14.10	10.9
.7	.343	6.08	4.80	13.83	10.9
.8	.528	7.06	5.76	13.53	11.0
.9	.729	8.04	6.72	13.22	11.1
1.0	1.000	9.02	7.70	12.91	11.0

In order to compare the influence of a change in P upon the solubility of calcite in water and in a calcium sulfate solution of constant concentration, we must make some allowance for the change in the latter which actually occurs when the solution is in contact with solid gypsum. This we have done by computing the quotient in the last column of Table VI; its degree of constancy proves that, for any value of P within this range, the ratio of solubility of calcite in a (dilute) salt solution of constant concentration to that in water is independent of the partial pressure of carbon dioxide. That this is valid follows from Equation 2, for by setting up the corresponding expression for a definite salt solution, and dividing one by the other, we find the ratio of solubilities to be equal to a quotient of corresponding activity coefficients, and this quotient we would expect to be, in general, independent of P. In other words, the solubility of calcite in a given salt solution, if measured at a single partial pressure of carbon dioxide, may readily be calculated for any other pressure through the corresponding slope of the curve in water alone. For this reason we did not trouble to make measurements in sodium chloride solutions except at a single pressure; Table V shows that the influence of salt concentration is very marked, the solubility in 1 molal sodium chloride being practically double that in absence of the salt.

The experimental data are also conveniently treated on the basis of the function $f(m)$. Equation 3 may be written

$$\log f(m) = \log \alpha + {}^1/_3 \log (K_2/K_1\gamma\lambda_C) - {}^1/_3 \log K_C$$

where it is evident that $f(m)$ varies directly as α, since the other terms are constant. As the activity coefficient α is dependent upon the ionic strength, it is of interest to plot the several experimental values of $\log f(m)$ against the square root of the ionic strength; when this is done, the lines for the calcium sulfate and sodium chloride solutions converge to, and then coincide with, the line representing the solubility in absence of other salts.

The value of $f(0)$, derived by extrapolation of this curve to zero ionic strength, is 87.5 ± 0.5. From Equation **3,** since α is now virtually unity, $f(0) = (K_2/K_1\gamma\lambda c)^{1/3}\,(1/K_C)^{1/3} = (\varphi_0)^{1/3}(1/K_C)^{1/3}$; the value of the first factor φ_0 is, from the work of Walker, Bray and Johnston: 310, and therefore K_C, the solubility product constant of calcite in terms of activities is 4.82×10^{-9} at 25°. The difference between this value and that calculated by McCoy and Smith[20] **(9.3×10^{-9})**, by Osaka[21] (7.24×10^{-9}) and by Mitchell[4] (5.88×10^{-9}) is attributable to the different values assumed for the constants and coefficients in the first factor in the equation above.

By applying the expression

$$\log f(0) + \log \alpha = \log f(m)$$

which is derived from Equation 3, to interpolated values of $\log f(m)$ at even values of the total ionic strength, we obtain the activity coefficients of calcium bicarbonate presented in Table VII; these, it may be noted, are higher than usual for salts of the unibivalent type.

TABLE VII

ACTIVITY COEFFICIENTS OF CALCIUM BICARBONATE FROM SOLUBILITY MEASUREMENTS AT 25°

μ =	**0.001**	**0.002**	**0.005**	**0.01**	**0.02**	
α =	**.96**	**.94**	**.91**	**.88**	.83	
μ =		**.05**	.08	.1	.2	**0.5**
In NaCl solns. α =		.84	**.70**	**.68**	**.51**	**.45**
In $CaSO_4$ solns. α =		.73	**.66**	...	...	...

In the experiments in which calcium sulfate was one of the solid phases in equilibrium with the solution, the data may be tested as to their agreement with the solubility product of calcium sulfate. Lewis and Randall[22] have compared the results obtained by Harkins and Paine[23] on the solubility of gypsum in the presence of $CuSO_4$, $MgSO_4$ and of KNO_3 by plotting against the ionic strength the ratio $1/m_\pm$ (the reciprocal of the mean molality of calcium sulfate) to γ (the activity coefficient of $MgSO_4$ at the same ionic strength). In our experiments the ionic strength varied only slightly from the average, $\mu = 0.072$ molal; at this strength we find the mean value of the ratio to be 183, as compared with 182 found by Lewis and Randall. This agreement is perhaps as close as can be expected in view of the fact that in one case the common ion is the cation, while in the other it is chiefly the anion.

[20] McCoy and Smith, THIS JOURNAL, **33,468 (1911).**

[21] Osaka, *Mem. Coll. Sci.* ***Kyoto,*** **5, 131 (1922).**

[22] **Ref. 17, p 376.**

[23] Harkins and Paine. THIS JOURNAL, **41,1160 (1919).**

The regularity of the log $f(m)$ curve for calcite, and the agreement of the reciprocal molality–activity coefficient ratio of gypsum with the value obtained by others, may be taken as evidence that the properties of the solid phases are unaltered under the conditions investigated. As a confirmatory test of the view that solid solution and compound formation do not occur under our conditions, it is of interest to consider the effect of the partial pressure of carbon dioxide on the ratio of carbonate ion to sulfate ion in the solution as suggested by Equation 4. A more convenient expression is obtained by dividing **3** by 4, as follows

$$\frac{1}{P}\frac{(Ca^{++})(HCO_3^-)^2}{(Ca^{++})(SO_4^=)} = \frac{(K_1\gamma\lambda_C)\,K_C}{(K_2)\quad K_G} = \varphi_0\frac{K_C}{K_G}$$

or

$$\frac{1}{P}\frac{\alpha^3[Ca^{++}][HCO_3^-]^2}{\beta^2[Ca^{++}][SO_4^=]} = \varphi_0\frac{K_C}{K_G}$$

where by canceling [Ca^{++}][24] and rearranging, we have

$$\frac{[HCO_3^-]^2}{[SO_4^=]} = P\frac{\beta^2}{\alpha^3}\varphi_0\frac{K_C}{K_G}$$

Owing to the slight effect of P upon the ionic strength of the solutions saturated with both calcite and gypsum, α and β are practically constant; a plot of the quotient $[HCO_3^-]^2/[SO_4^=]$ against P should therefore be a smooth, almost linear curve, as it proves to be in spite of the fact that irregularities in the experimental data are accentuated by the presence of a squared term in the quotient. Any marked change in curvature would indicate some change in the solid phases; from its absence we feel justified in concluding that the stable crystalline phases, under the conditions of our measurements, are calcite and gypsum, and that no solid solution or double salt appears. It may be mentioned that there is some evidence[25] that, under similar conditions, aragonite and calcium sulfate do to some extent (apparently up to about 0.7% $CaSO_4$) form solid solutions, an observation which may be of considerable geological significance.

Summary

1. The solubility of calcite at 25° in water saturated with carbon dioxide at partial pressures ranging from 0.0003 to 1.0 atm. has been determined. The solubility product constant of calcite at 25°, in terms of activities, proved to be 4.8×10^{-9}.

2. An apparatus is described which facilitates solubility determinations in systems in which the composition both of the liquid and the gas phase must be ascertained.

3. Measurements are presented of the solubility of calcite at 25° in

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[24] As α and β are the mean activity coefficients of bicarbonate and sulfate, respectively, the individual ion activities being unknown, it is therefore preferable to cancel the calcium term as a concentration rather than as an activity.

[25] Adverted to earlier, and also in a previous paper, ref. 2f, pp. 508–509.

solutions of calcium sulfate and of sodium chloride under partial pressures of carbon dioxide ranging from 0.1 to 1.0 atm.; from these results the activity coefficients of calcium bicarbonate have been derived. The concentrations of calcium sulfate and carbonate in the solutions saturated with both gypsum and calcite afford no indication of any alteration in the nature of either of these solid phases under these conditions.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SOLUBILITY OF MAGNESIUM CARBONATE (NESQUEHONITE) IN WATER AT 25° AND PRESSURES OF CARBON DIOXIDE UP TO ONE ATMOSPHERE[1]

BY WALTER D. KLINE[2]

RECEIVED MARCH 20, 1929 PUBLISHED JULY 5, 1929

The measurements presented in this paper were made with a view to securing more reliable data than were then available[3] on the solubility of magnesium carbonate (nesquehonite, $MgCO_3 \cdot 3H_2O$) in water at 25°, for a range of partial pressures of carbon dioxide extending downward from one atmosphere, and on the limiting pressure at which magnesium hydroxide becomes the stable solid phase in equilibrium with the solution. Such data are of interest in connection with the control of the conditioning of many natural waters and the preparation of pure magnesia, and are a necessary preliminary step toward the solution of the puzzling problem of the mode of formation of dolomite.

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[1] From the dissertation presented by W. D. Kline to the Graduate School of Yale University, June, 1923, in candidacy for the degree of Doctor of Philosophy.

[2] Loomis Fellow, 1921–1922; du Pont Fellow, 1922–1923.

[3] (a) Engel, *Ann. chim. phys.*, 13, *344* (1888), determined the equilibrium between $MgCO_3 \cdot 3H_2O$, water and (1) CO_2 at pressures of 0 5–6 atm. at 12°; (2) CO_2 at 1 atm. and several temperatures up to 50°. (b) Leather and Sen, *Memoirs Dept. Agric. India* Chem. Series **3,** No. 8 (1914); sundry measurements, not very reliable. (c) Mitchell, *J. Chem. Soc.*, *123*, 1887 (1923), measured the solubility at 25° at pressures of 6–21 atm. of CO_2. (d) Haehnel, *J. prakt. Chem.*, 108, 61 (1924), made measurements at 18° and pressures 2–56 atm. of CO_2; and at **34** atm. over the temperature range 0–60°. Since, however, the solubility at 18° becomes constant at pressures exceeding 18 atm., this is evidence of a new solid phase, bicarbonate presumably; hence the temperature coefficient of solubility at 34 atrn. does not apply to our solid phase. (e) Cf. also Johnston, THIS JOURNAL, 37,2001 (1915).

In order to compare these several results with ours, they were recalculated in terms of moles per kilo of water by assuming that (a) the solution may be regarded as all bicarbonate; (b) the temperature coefficient of specific gravity of a solution of $Na(HCO_3)$ (given for 18° in "International Critical Tables") is the same as that of water; (c) the ratio of specific gravity of equimolal solutions of $Mg(HCO_3)_2$ and $NaHCO_3$ is the same as that of equimolal solutions of $MgCl_2$ and NaCl. The solubility at 25° was interpolated by means of a plot of log m against $1/T$.

The equations developed in the preceding paper for solutions saturated with calcium carbonate apply equally to magnesium carbonate if for K_c we substitute $K_M = (Mg^{++})(CO_3^{--})$; so that in this case $f(m)$, which is evaluated as $P^{1/3}/m$, is equal to $\alpha\sqrt[3]{K_2/K_1K_M\gamma\lambda c}$.

The form of magnesium carbonate stable in contact with its aqueous solution at 25° is the trihydrate, nesquehonite, $MgCO_3{\cdot}3H_2O$. Numerous basic carbonates have been reported in the literature, but it is doubtful whether any of these correspond to a definite crystalline compound. That some of them at least are indefinite mixtures has been shown by microscopic[4] and by x-ray[6] methods; the probability that all are likewise indefinite may be inferred from a consideration of the factors which determine the stability of hydroxide and of carbonate in aqueous solution. For with decreasing partial pressure of carbon dioxide there corresponds an increase in the ratio $(OH^-)/(CO_3^-)$ and, owing to the fact that magnesium hydroxide is much less soluble than the carbonate, there is a pressure below which the hydroxide becomes the stable solid phase; this limiting pressure was in a previous paper[3]" estimated at about 0.00037 atm. of carbon dioxide, slightly greater than the proportion ordinarily present in air. It is therefore likely that in the precipitation of magnesium carbonate some proportion of hydroxide will also appear unless care is taken to keep the effective concentration of CO_3^{--} high and of OH^- correspondingly low. In any case, if there be any range of carbon dioxide pressure within which a basic carbonate is stable at 25°, this range must lie between the zones of stability of the normal carbonate and the hydroxide; no definite indication of this was observed in the present work.

Experimental

Kahlbaum's magnesium carbonate trihydrate was used as the solid phase in this work, since its analysis and its solubility proved to be identical with those of material prepared with special precautions to obviate contamination by magnesium hydroxide and by double carbonates of magnesium with the alkali metals. Equilibrium was established in three to five days by bubbling mixtures of carbon dioxide and air in constant proportions through conductivity water in contact with the finely divided solid in the manner used for studying the solutions of alkali carbonates;[6] the methods there described were employed in analyzing gas phase and solution. In the determination of total base no attempt was made to correct for incomplete saturation of the titration mixture with carbon dioxide, as the correction was apparently less than the general experimental error. In the determination of bicarbonate, made on 15–20 g.

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[4] E. S. Larsen, *Am. Mineralogist*, 2, 3 (1917).

[5] G. R. Levi, *Ann. chim. appl.*, 14, 265 (1924).

[6] **Walker, Bray** and **Johnston,** THIS JOURNAL, 49, 1235 (1927).

of the equilibrated solution, the excess of baryta added was limited to 20 milli-equivalents; otherwise the end-point, on titration with acid, was uncertain owing to the gradual re-solution of the magnesium hydroxide precipitated by the excess of baryta.

Table I lists the mean analytical results in the first three columns, respectively, the partial pressure of carbon dioxide, P, and the millimolality (millimoles per kilo water) of magnesium, m_1, and of bicarbonate, m_2. The figures in the fourth column are derived from the relation $[CO_3^{--}] = m_3 = m_1 - {}^1/_2\, m_2$; the ionic strength ($\mu$) in the fifth column is from the data in Cols. 2, 3 and 4; and the values of $[OH-]$, in the last column, as will be described later.

TABLE I

OBSERVED MEAN MOLALITIES OF SOLUTIONS IN EQUILIBRIUM WITH A SERIES OF PRESSURES OF CARBON DIOXIDE AT 25°

P	$[Mg^{++}] \times 10^3$, m_1	$[HCO_3^-] \times 10^3$, m_2	$[CO_3^{--}] \times 10^3$, m_3	μ	$[OH^-] \times 10^5$, m_4	Solid phase
0.000107	4.33	4.88	1.89	0.0149	3.84	$Mg(OH)_2$
.000113	4.45	5.01	1.95	.0153	3.73	
.000170	5.77	7.45	2.05	.0194	3.69	
.000179	5.93	7.63	2.12	.0199	3.59	
.000197	6.58	7.95	2.61	.0224	3.40	
.000210	7.08	8.06	3.05	.0243	3.23	
.000233	7.80	8.37	3.61	.0270	3.03	
.000251	8.07	8.55	3.80	.0280	2.87	
.000310	10.13	11.84	4.21	.0346	3.22	
.000376	12.96	14.04	5.94	.0448	3.14	
.000380	13.55	14.32	6.39	.0470		
.000510	14.37	17.10	5.82	.0489		$MgCO_3 \cdot 3H_2O$
.000680	15.12	18.72	5.76	.0511		
.000845	15.66	19.90	5.71	.0527		
.000887	15.93	20.46	5.70	.0535		
.000930	16.24	21.19	5.65	.0544		
.00160	18.59	26.98	5.10	.0609		
.00334	22.10	35.48	4.36	.0707		
.00690	25.07	44.68	2.73	.0779		
.0150	31.27	60.22	1.16	.0950		
.0432	46.01	89.98	1.02	.1390		
.1116	62.66	123.6	0.85	.1889		
.9684	213.5	426.9	..	.6405		

From these data it is obvious that with increase of partial pressure the molality of carbonate increases to a well-defined maximum, when P is about 0.00038 atm., and then decreases more gradually. Corresponding to this it was observed that the appearance of the crystals of $MgCO_3 \cdot 3H_2O$ remained unchanged throughout the course of the experiment at all of the pressures greater than 0.00038; but that at lower pressures the solid phase appeared to become very fine-grained—indicating therefore a change from carbonate to hydroxide, the duration of the experiments being insufficient to ensure complete conversion of the solid phase from carbonate to hydroxide. Accordingly we shall take the transition pressure (P_{tr}) as 0.0004 atm. at 25°, and consider separately the two regions in which carbonate or hydroxide, respectively, is the stable solid phase.

Evaluation of K_M, the Activity-Product Constant of **$MgCO_3{\cdot}3H_2O$.**—By definition $K_M = (Mg^{++})(CO_3^{--}) = m_1m_3\alpha_1\alpha_3$, where m_1 and m_3 represent gross molalities, and α_1 and α_3 the activity coefficients. When the experimental values of log m_1m_3 for pressures above 0.0004 are plotted against $\mu^{1/2}$ they lie—particularly at the more dilute end—on a smooth curve with diminishing curvature, becoming a straight line with the slope 4 (in accordance with the Debye–Hückel theory); the point at which this line cuts the axis $\mu^{1/2} = 0$ (where accordingly α_1 and α_3 are each unity) corresponds to $K_M = 1.1 \times 10^{-5}$.

It may also be evaluated from a plot of log $m_1m_2^2/P$ against $\mu^{1/2}$, extrapolated finally as a straight line of slope **3;** the intersection with the axis corresponds to log K_M + log φ_0, φ_0 being 310.[7] This leads to $K_M = 0.8 \times 10^{-5}$; but we would assign a greater weight to the other value, because this second function is very sensitive. Accordingly we shall adopt for K_M at 25° the value 1×10^{-5}.

Evaluation of K_H, the Activity-Product constant of **$Mg(OH)_2$.**—With a knowledge of K_M and of the transition pressure P_{tr} we may evaluate K_H from the relation

$$K_H = \frac{K_W^2}{\gamma\lambda c K_1 K_2} \times \frac{K_M}{Pt,}$$

which is readily derived by combining[8] the equations of the preceding paper with the definitions $K_H = (Mg^{++})(OH^-)^2$, K_W = (Hf)(OH−). Substituting the values of the several coefficients, we obtain

$$K_H = 2.20 \times 10^{-10} \times \frac{1 \times 10^{-5}}{0.0004} = 5.5 \times 10^{-12}$$

This also may be evaluated in another way. The molality of hydroxyl ion (m_4) is calculated in each case from m_2, P and the appropriate constant~; the resulting values are listed in the last column of Table I. When log $m_1m_4^2$ is plotted against $\mu^{1/2}$ and extrapolated, as before, on an initial slope of **3,** we find an intercept corresponding to $K_H = 2.7 \times 10^{-12}$.

These two values agree as well as could be expected under the circumstances; we consider the higher to be the more reliable. This constant has been given as 12×10^{-12} at 18°, derived from conductivity measure-

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[7] Cf. preceding paper and ref. 6.

[8] This equation was developed, in slightly different notation, in ref. 3 *e*.

[9] As discussed in ref 6; $[OH^-] = 8.42 \times 10^{-7}[HCO_3^-]/P$.

ments of saturated solutions of magnesium hydroxide[10] and from hydrogen electrode determinations;[11] that it is higher than ours is to be ascribed in part to the difference of temperature (the solubility of magnesium hydroxide is thought to decrease with increase of temperature) and to the method of calculation, but may be largely due to the fact that such direct determinations tend to be high unless carbon dioxide is rigorously excluded from the solution. It may be added that Greenfield and Buswell,[12] from observations of the PH at which magnesium hydroxide is precipitated by alkali, conclude that K_H should be slightly less than 12×10^{-12}.

The general agreement of these values corroborates the view that there is at 25° no definite stable basic carbonate with a field between that of hydroxide and that of normal carbonate, for by substituting the values of K_H and K_M in the expression given above, we derive a value of P_{tr} of the same order as that observed; whereas the assumption of any basic carbonate (for instance, $MgCO_3 \cdot Mg(OH)_2$ or $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$), leads to a calculated transition pressure so much larger as to be irreconcilable with that observed.

Summary

The equilibrium in solutions of magnesium carbonate at 25° has been investigated over a range of pressures of carbon dioxide from 1 to 0.0001 atmosphere. The carbonate is stable down to 0.004 atm., below which the hydroxide is stable; no indication of definite basic carbonates was observed. The activity product constant of magnesium carbonate at 25° is taken as 1×10^{-5}; that of magnesium hydroxide similarly as 5×10^{-12}. Interpolated values of the molality of magnesium in the solution saturated with the carbonate at 25° for a series of values of the partial pressure (in atrn.) of carbon dioxide are appended.

P	[Mg]	P	[Mg]	P	[Mg]
0.001	0.0178	0.3	0.117	2	0.287
.01	.0270	.5	.152	5	.384
.05	.0489	.7	.181	10	.471
.1	.0660	1.0	.217	15	.526

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[10] Dupré and Bialas, *Z. angew. Chem.*, *16*, **55 (1903).**

[11] Gjaldbaek, *Z. anorg. allgem. Chem.*, **144, 145,** *269* **(1924).**

[12] **Greenfield and** Buswell, This Journal, **44, 1435 (1922).**

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ROYAL VETERINARY AND AGRICULTURAL COLLEGE OF COPENHAGEN]

THE KETONIC DECOMPOSITION OF BETA-KETO CARBOXYLIC ACIDS

BY KAI JULIUS PEDERSEN

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It is well known that β-keto carboxylic acids, *e.g.*, acetoacetic acid, split off carbon dioxide according to the scheme

$$CH_3COCH_2COOH \longrightarrow CH_3COCH_3 + CO_2$$

and that the cleavage is catalyzed by certain amines. This so-called ketonic decomposition is characteristic of β-keto acids, neither a- nor γ-acids showing any appreciable decomposition. Thus pyruvic and levulinic acids are stable. Unless both the a-hydrogen atoms are substituted, the β-keto acids consist of a mixture of two tautomers, a keto form and an enol form; for instance, in the case of acetoacetic acid

$$CH_3COCH_2COOH \rightleftharpoons CH_3COH{:}CHCOOH$$

Opinions differ as to whether the keto or the enol form is the unstable form. The present work is an attempt to solve this problem. On the suggestion of Professor N. Bjerrum the α,α-dimethylacetoacetic acid, which exists only in the keto form, was investigated. If only the enol form of β-keto acids is unstable, the α,α-disubstituted acid must be stable in aqueous solution.

The kinetics of the ketonic decomposition of β-keto acids and the catalysis by amines have been investigated several times. G. Bredig and his school[1,2,3] studied camphorcarboxylic acid and a-bromocamphorcarboxylic acid

$$C_8H_{14}\left\langle\begin{array}{l}CO\\ |\\ CHCOOH\end{array}\right. \quad \text{and} \quad C_8H_{14}\left\langle\begin{array}{l}CO\\ |\\ CBrCOOH\end{array}\right.$$

While the former has a keto and an enol form, the latter is purely ketonic. It was first shown by Fajans[3] that the latter splits off carbon dioxide and that its decomposition is catalyzed by amines. For camphorcarboxylic acid it has thus been established that the keto form can decompose.

The decomposition of acetoacetic acid has been studied by I,. Pollak,[4] N. O. Engfeldt,[5] E. M. P. Widmark,[6] H. v. Euler[7] and G. Ljunggren.[8]

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[1] G. Bredig, Z. *Elektrochem.*, 24, 285 (1918).

[2] Pastanogoff, Z. *physik. Chem.*, 112,448 (1924).

[3] K. Fajans, *ibid.*, 73, 25 (1910).

[4] Pollak, *Hofmeisters Beitrage*, 10, 234 (1907).

[5] Engfeldt, "Beiträge zur Kenntnis der Biochemie der Acetonkörper," Dissertation, Lund, 1920.

[6] Widmark, *Acta Med. Scand.*, *53*, 393 (1920); *Skand. Arch. Physiol.*, 42, 43 (1922).

[7] H. v. Euler, Z. *anorg. Chem.*, 147, 295 (1925).

[8] Ljunggren, "Katalytisk Kolsyreavspjälkning ur Ketokarbonsyror," Dissertation. Lund, 1925.

It has been shown that the rate of decomposition follows the law

$$-\frac{dc}{dt} = k'_m c(1 - \alpha) + k'_i c\alpha \tag{1}$$

where c is the concentration of acetoacetic acid, α its degree of dissociation and k'_m and k'_i are velocity constants for the decomposition of the undissociated acid and the ion. From experiments in buffer solutions it is possible to calculate the dissociation constant of acetoacetic acid (Widmark). Ljunggren's results are given in Table VI at the end of this paper. Widmark and Ljunggren have found that amines only catalyze when the PH of the solution is kept within a limited interval, while the amines are inactive in strong acid and alkaline solutions. This they explain by assuming that either the neutral amine reacts with the undissociated acetoacetic acid or the positive ammonium ion with the' acetoacetate ion. It is impossible to distinguish between these possibilities on the basis of kinetic experiments. Ljunggren has found that only primary amines are good catalysts. Secondary and tertiary amines give only small effects.

A similar reaction, the decomposition of acetone-dicarboxylic acid

$$CO(CH_2COOH)_2 \longrightarrow CO(CH_3)_2 + 2\,CO_2$$

has recently been studied by E. O. Wiig.[9] He determined the velocity of the decomposition in water, aniline and various alcohols and also the effect of catalysts. Wiig does not take into account the dissociation equilibrium of acetone-dicarboxylic acid. This acid is fairly strong. According to Angeli[10] its dissociation constant in aqueous solution is 0.79×10^{-3}. Consequently its aqueous solution contains both undissociated acid and univalent ion, and these will probably decompose with different velocities. It seems to the author that this is the simplest explanation of Wiig's experiments in aqueous hydrochloric acid, where he finds that the velocity constant at first decreases and then remains constant with increasing concentration of hydrochloric acid. He explains the retardation by assuming that hydrogen chloride adds to the keto group, forming a stable compound, but it is simpler to assume that the undissociated acetone-dicarboxylic acid decomposes somewhat more slowly than its univalent ion. Addition of hydrochloric acid to the solution causes a depression of the dissociation until the acid is completely undissociated. On p. 970 Wiig takes into account the hydrogen-ion concentration due to the dissociation of the carbonic acid formed by the reaction in an aqueous solution of acetone-dicarboxylic acid, while he disregards the much greater hydrogen-ion concentration from the acetone-dicarboxylic acid itself.

Experimental Part

The velocity of the ketonic decomposition of α,α-dimethylacetoacetic acid was determined at the temperature 18.00° by means of an apparatus

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[9] **Wiig,** *J. Phys. Chem.,* 32, 961 (1928).

[10] Angeli, *Gazz. chim. ital.,* II, *22,* 31 (1892).

described by J. N. Brönsted.[11,12] The pressure of carbon dioxide above the solution in the closed apparatus is measured during the reaction. Experiments were made in solutions of hydrochloric acid sufficiently concentrated to make the dimethylacetoacetic acid practically completely undissociated, and in glycolate and acetate buffer solutions, where the dimethylacetoacetic acid is partially dissociated.

Impurities of acetoacetate and monomethylacetoacetate were removed from the ethyl ester of α,α-dimethylacetoacetic acid (Kahlbaum) by shaking for an hour with an equal volume of 25% potassium hydroxide solution.[13] After separation from the aqueous layer and two distillations it boiled at 184–185° (boiling point found by Perkin[14] 184.8–185.0°).

The amount of the ethyl ester used for an experiment (0.001-0.002 mole) was weighed out, an excess of sodium hydroxide added and the mixture was left at room temperature until the next day. Rough determinations of the rate of hydrolysis of the ester had shown that this was sufficient for practically complete hydrolysis. Acid was added, the solution diluted to 100 cc. and poured into the reaction flask in the apparatus.

Experiments in Solutions of Hydrochloric Acid.—The reaction follows the unimolecular law

$$-k_m t = \log c + \text{constant} \tag{2}$$

where k_m is the velocity constant expressed by means of decadic logarithms, t is the time in minutes and c the concentration of dimethylacetoacetic acid at the time t. P denotes the difference, $p_\infty - p$, between the pressure p_∞ above the solution after the reaction is complete and the pressure p at the time t. As P and c are proportional during the reaction, $c = fP$ and Equation 2 may be written

$$-k_m t = \log P + \text{constant}$$

k_m was computed according to this equation by plotting log P against t; f does not enter into the calculations when the reaction follows the unimolecular law. Only when this law does not hold, as in experiments in buffer solutions, is a knowledge of the value of f necessary. f can be calculated from the known concentration of the reacting substance before the experiment (c_0) and the total increase in pressure during the experiment (P_0); $f = c_0/P_0$.

The results of the experiments in hydrochloric acid are given in Table I. Owing to the method of preparation of the solutions they all contain a little ethyl alcohol (<0.02 M) originating from the ester. By comparison of Expts. 1 and 2 with 4, where extra alcohol has been added, it is seen that 0.02 M alcohol can have no detectable effect. Hydrochloric acid,

[11] Brönsted and King, THIS JOURNAL, 47, 2523 (1925).

[12] Brönsted and Duus, Z. *physik.* Chem., 117, 299 (1925).

[13] A. Michael, Ber., 38, 2096 (1905).

[14] Perkin, J. Chem. *Soc.*, 83, 1231 (1903).

sodium chloride and glycolic acid all have a small accelerating effect. If we assume that the effects vary linearly with the concentrations of the substances, and that they are independent of one another, we get the following values for the increase in k_m per mole/liter of added substance: hydrochloric acid, 50×10^{-6}; sodium chloride, 37×10^{-6}; undissociated glycolic acid, 25×10^{-6}. By means of these data we find by extrapolation the velocity constant for the decomposition of undissociated dimethylacetoacetic acid in pure water, $k_{m0} = 723 \times 10^{-6}$.

TABLE I

THE VELOCITY OF DECOMPOSITION OF DIMETHYLACETOACETIC ACID IN HYDROCHLORIC ACID

No.	Concn. of dimethylacetoacetic acid, c_0	Concn. of HCl	Concn. of NaCl	Other substances	$k_m \times 10^{-6}$
1	0.01801	0.175	0.040	....	729
2	.01562	.108	.040	....	730
3	.01604	.551	.040	....	752
4	.01747	.175	.040	0.20 M C_2H_5OH	724
5	.01465	.108	.640	....	752
6	.01576	.108	.040	1.18 M $CH_2OHCOOH$	759

Experiments in Buffer Solutions.—These measurements were made in order (1) to determine the dissociation constant of dimethylacetoacetic acid, (2) to obtain an idea of the velocity of decomposition of the dimethylacetoacetate ion and (3) to examine whether the reaction like the decomposition of the acetoacetic acid itself is catalyzed by amines.

The velocity of decomposition in a buffer solution depends on the degree of dissociation (α) of the dimethylacetoacetic acid at the P_H of the solution. Equation 1 holds as for acetoacetic acid.

Glycolate buffer solutions were chosen for the determination of the dissociation constant of dimethylacetoacetic acid because this constant and that of glycolic acid are of the same order of magnitude. The ratio $L = K_D/K_G$, where K_D and K_G are the concentration dissociation constant of dimethylacetoacetic acid and glycolic acid, is presumably almost independent of the salt concentration even in fairly concentrated solutions, although the dissociation constants themselves are very sensitive to salt. In order to minimize the change in hydrogen-ion concentration due to the disappearance of the dimethylacetoacetic acid, rather concentrated buffer solutions were used. A correction formula was also applied.

It will be shown later that for experiments in glycolate buffer solutions the decomposition of the dimethylacetoacetate ion is negligible compared with that of the undissociated acid, at least when no catalyst is present. Equation 1 reduces to

$$\frac{dP}{Pdt} = -k'_m(1-\alpha) \tag{3}$$

α increases during the decomposition. α_0 denotes its value at the time ∞ when the concentration of dimethylacetoacetic acid is 0. We want to calculate the velocity constant

$$k' = k'_m\,(1 - \alpha_0) \qquad (4)$$

corresponding to this concentration.

From the mass action law we get

$$\frac{a + \alpha c}{b - \alpha c}\,\frac{\alpha}{1 - \alpha} = L$$

where a and b are the stoichiometric or final concentrations of glycolic acid and sodium glycolate, respectively. Hence

$$\alpha = \frac{L(b - \alpha c)}{a + Lb - (L - 1)\alpha c} \text{ and } \alpha_0 = \frac{Lb}{a + Lb} \qquad (5)$$

$$\alpha_0 - \alpha = \frac{L(a + b)\alpha c}{(a + Lb - (L - 1)\alpha c)\,(a + Lb)}$$

We now use as an approximation in the numerator $\alpha = \alpha_0$ and in the denominator c = 0. Using $c = f \times$ P and (5), we get

$$\alpha_0 - \alpha = \frac{L^2b(a + b)fP}{(a + Lb)^3}$$

From (3), (4) and (5) we get

$$-\frac{dP}{Pdt} - k' = k'_m\,(\alpha_0 - \alpha) = \frac{L^2b(a + b)f \times k'_m}{(a + Lb)^3} \times P$$

$$= \frac{L^2b(a + b)f \times k'}{(a + Lb)^2a}\,P = A \times k' \times P$$

where A denotes

$$\frac{L^2(a + b)b \times f}{(a + Lb)^2 \times a}$$

Hence by integration

$$\log_e\left(\frac{1}{P} + A\right) = k't + \text{constant, or}$$

$$\log_{10}\left(\frac{1}{P} + A\right) = kt + \text{constant} \qquad (6)$$

In order to use this formula we require an approximate value of L. We find this by plotting log P against t. We get in this way a curve which deviates only slightly from a straight line. The slope gives an approximate value of $k = k_m(1 - \alpha_0)$. We now calculate L from Equation 5. Knowing L we can calculate A. We finally plot log $(1/P + A)$ against t and find k. The calculation of an experiment has been given in Table II.

In Table III are given the values of k computed in this way for glycolate buffer solutions.

It has been found in the experiments in hydrochloric acid that sodium chloride and undissociated glycolic acid have a small accelerating effect on the decomposition of the undissociated dimethylacetoacetic acid and the magnitude of these effects has been found. From a comparison of Expts. 7 to 10 or 11 and 12 (Table III) we see that sodium glycolate has a

TABLE II

EXPERIMENT NO. 11

$c_0 = 0.01361$; a = 0.2924; b = 0.2009; f = 0.01361/9.11 = 0.00149; L = 2; A = 0.0042.

t, min.	P (cm. Hg)	$\log\left(\frac{1}{P}+A\right)$	t, min.	P (cm. Hg)	$\log\left(\frac{1}{P}+A\right)$
0	9.11^a	...	350	7.01	0.167
23	9.02	0.061	380	6.87	.176
120	8.33	.094	395	6.78	.181
153	8.12	.105	453	6.50	.199
178	7.98	.112	1505	3.00	.528
212	7.78	.123	1562	2.88	.546
240	7.60	.133	1606	2.77	.562
276	7.40	.144	1750	2.50	.607
315	7.20	.156	1795	2.40	.624

$k = 315\ 10^{-6}$

[a] Extrapolated

TABLE III

THE VELOCITY OF DECOMPOSITION OF DIMETHYLACETOACETIC ACID IN GLYCOLATE BUFFER SOLUTIONS

No.	Concn. of glycolic acid, a	Concn. of glycolate, b	k X 10^6, exp.	L*	k_m X 10^6	$1 - \alpha_0$	L	k X 10^6, calcd.
7	0.1937	0.2009	243	1.925	759	0.320	2.05	244
8	.1937	$.2009^a$	250	1.900	774	.323	2.02	248
9	.3858	.4034	253	1.815	795	.318	2.05	254
10	.581	.603	265	1.720	831	.319	2.06	267
11	.2924	.2009	315	1.920	761	.414	2.06	317
12	.5847	.4018	331	1.790	800	.414	2.06	333
13	.7804	.4034	396	1.695	805	.492	2.00	392
14	.782	.402	396	1.705	805	.492	2.00	392
15	.572	.020	680	...	740	.920	..	692
16	1.164	.020	725	...	755	.960	..	730

[a] Added 0.40 M NaCl. Mean value L = 2.04.

similar effect. Although $1-\alpha_0$ is almost constant within these experiments, k varies much more than can be accounted for by the small effect of the undissociated glycolic acid and the sodium chloride. We first calculate L without taking into account the effect of the sodium glycolate. We denote by * the data in the calculation of which this effect has been neglected.

$$1 - \alpha_0^* = \frac{k}{k_m^*} \qquad L = \frac{a}{b} \times \frac{\alpha_0^*}{1 - \alpha_0^*} \tag{7}$$

where $k_m^* = (723 + 37\,c_{\mathrm{NaCl}} + 25\,a) \times 10^{-6}$.

We assume that the effect of the sodium glycolate on k_m is proportional to its concentration, $k_m = k_m^* + \beta b$. By introduction in (7)

$$L^* = \frac{a}{b} \times \frac{k_m - \beta b - k}{k} = \frac{a}{b}\,\frac{k_m - k}{k} - \beta\,\frac{a}{k}$$

$$L^* = L - \beta \times \frac{a}{k} \tag{8}$$

From this equation we see that we can find β by plotting L^* against a/k. See the diagram. The value of the slope is $-\beta = -155 \times 10^{-6}$. We can now calculate k, $1 - \alpha_0$ and L. The values are given in Table III. The mean value of L is 2.04. Using this value for L and

$$10^6 \times k_m = 723 + 37\, c_{\mathrm{NaCl}} + 25\, a + 155\, b$$

we calculate the k values given in the last column of Table III. They are in good agreement with the experimental values.

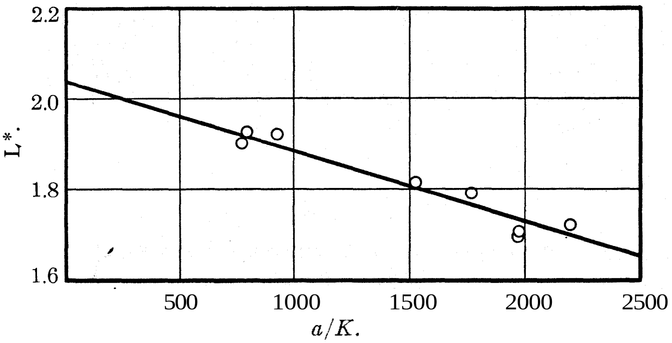

Fig. 1.—Graphical determination of the effect of sodium glycolate on the rate of decomposition of undissociated dimethylacetoacetic acid, Equation 8. The slope is $-\beta = -155 \times 10^{-6}$.

We have now determined the ratio between the dissociation constants of dimethylacetoacetic acid and glycolic acid, L = 2.04 at 18°. The dissociation constant of glycolic acid has been determined by J. Boeseken and H. Kalshoven.[15] They found at 25° the value 1.54×10^{-4} for dilutions from 4 to 512 liter/mole. It is permissible to use the same value at 18°, because the dissociation constants of weak acids in general do not vary much with the temperature. We thus find for dimethylacetoacetic acid the dissociation constant 3.14×10^{-4}.

In order to get an idea of k_i, the velocity of the decomposition of the dimethylacetoacetate ion, some measurements were made in acetate buffer solutions, where the dimethylacetoacetic acid is almost completely dissociated (Table IV). In the calculation of the velocity constant k Equation 6 has been applied. By means of the dissociation constant ratio for dimethylacetoacetic and acetic acid, $L = K_D/K_A = (3.14 \times 10^{-4})/(1.80 \times 10^{-5}) = 17.5$, $1-\alpha_0$ is calculated. If we neglect the effect of the medium (acetic acid and sodium acetate) on the decomposition of the undissociated dimethylacetoacetic acid, we can calculate $k_{m0}\,(1 - \alpha_0)$, the part of k which is due to the decomposition of undissociated dimethylacetoacetic acid. The part of k which is due to the decomposition of the ion is probably smaller than the difference given in the last column of Table IV, because

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[15] Boeseken and Kalshoven, Rec. *trav. chim.*, 37, 130 (1918).

we have used k_{m0} instead of k_m. Thus the velocity constant for the decomposition of the dimethylacetoacetate ion k_i is smaller than 4×10^{-6}, while that for the undissociated acid is $k_{m0} = 723 \times 10^{-6}$. In the experiments in glycolate buffers, k_i has been neglected. The results will only be slightly different if we use $k_i = 4 \times 10^{-6}$.

TABLE IV

THE VELOCITY OF DECOMPOSITION OF DIMETHYLACETOACETIC ACID IN ACETATE BUFFER SOLUTIONS

No.	Concn of acetic acid	Concn. of sodium acetate	k × 10^6	$1 - \alpha_0$, calcd.	$k_{m0}(1 - \alpha_0)10^6$	Diff.
17	0.300	0.300	44	0.059	42	2
18	.300	.600	25	.029	21	4
19	.500	.500	46	.059	42	4

The Catalysis by Amines.—In Table V are given two experiments in which the catalysis of an amine, aniline, was examined. The results are only approximate because no correction has been made for the change in α during the reaction. Nevertheless, it is clear from a comparison of the last two columns of Table V that aniline has a very great accelerating effect. In the calculation of α the value found by Bronsted and Duus[12] for the acid strength[16] of the anilinium ion

$$K_{C_6H_5NH_3^+} = \frac{(C_6H_5NH_2)\ (H^+)}{(C_6H_5NH_3^+)} = 2.06 \times 10^{-5}$$

has been used. The ratio $L = K_D/K_{C_6H_5NH_3^+}$, unlike L for glycolic acid, is highly salt sensitive. The α-values calculated in this way are therefore only rough approximations.

TABLE V

THE CATALYTIC EFFECT OF ANILINE ON THE DECOMPOSITION OF DIMETHYLACETOACETIC ACID

No.	Concn. of acetic acid	Concn. of sodium acetate	Concn of aniline hydrochloride	Concn of aniline	k × 10^6	k × 10^6 calcd without catalysis
20	0.500	0.500	0 0986	0 122	1310	40
21	.000	.000	.0585	.0426	680	61

Discussion

In Table VI the velocity constants found by Ljunggren for acetoacetic acid are given together with the constants found in the present work for dimethylacetoacetic acid. Ljunggren worked at 37 and 25°. His values have been extrapolated to 18° by means of the formula d log $k/\mathrm{d}(1/T)$ = constant, where T is the absolute temperature. As seen from the table, the undissociated dimethylacetoacetic acid, that is, a pure ketone, at 18° decomposed 4.5 times as quickly as the undissociated acetoacetic acid. At 18° dimethylacetoacetic acid decomposes with the same velocity as

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[16] J. N. Bronsted, *Rec. trav. chim.*, 42, 718 (1923); *J. Phys. Chem.*, 30, 777 (1926)

acetoacetic acid at about 29°. It has thus been shown that the keto form is unstable. Probably only the keto form decomposes.

TABLE VI

ACETOACETIC AND DIMETHYLACETOACETIC ACID. VELOCITY CONSTANTS FOR THE KETONIC DECOMPOSITION (DECAD. LOG., MIN.$^{-1}$) AND DISSOCIATION CONSTANTS

	Acetoacetic acid (Ljunggren)			Dimethylacetoacetic acid,
	37°	25°	18° (extrap.)	(K. J. P.) 18°
Undissociated acid $k^0_m 10^6$	2080	430	161	723
Ion $k_i \times 10^6$	38.5	8.95	3.6	<4
Dissociation constant	2.04×10^{-4}	2.21×10^{-4}	2.29×10^{-4}	3.14×10^{-4}

Engfeldt[5] has by means of the bromination method of K. H. Meyer[17] determined the amount of ketone and enol in acetoacetic acid dissolved in water. Bromine reacts instantaneously with the enol form while it has no effect on the keto form. The accuracy of the analysis is not great owing to the formation of enol from the ketone during the analysis. Engfeldt therefore considers his results as being only rough approximations. He finds that undissociated acetoacetic acid (free acid + an excess of hydrochloric acid) consists of 18% keto form and 82% enol form. This result is not confirmed by a work which the author is doing on the applicability of the bromination method for the enol determination in aqueous solutions of acetoacetic acid and ester and similar substances. This together with a study of the velocity of the reaction ketone ⟶ enol will be the subject of a later publication. It was found that an aqueous solution of acetoacetic acid contains only very little enol, less than 1%.

As a result of the present work the following hypothesis is suggested. Only the keto form of β-keto carboxylic acids undergoes the ketonic decomposition. The amines which catalyze the reaction form an intermediate compound of unknown constitution with the keto form (enol $\rightleftarrows$ ketone $\rightleftarrows$ ketone-catalyst), thus reducing the concentration of both enol and ketone. The intermediate compound splits off carbon dioxide much more quickly than the free keto form.

The α,α-disubstituted acetoacetic acid is especially suited for the study of the catalysis, the non-occurrence of enol making this case simpler than that of the ordinary acetoacetic acid. A theory of the decomposition and catalysis must take into account that only β-keto acids show the ketonic decomposition with appreciable velocity, and that only the primary amines are good catalysts, while the secondary and tertiary amines have a moderate or almost no effect.

The work is being continued and it is hoped to give a further test of the above hypothesis in a later publication.

In conclusion I wish to thank the Carlsberg Poundation for a grant which has defrayed the expenses of the apparatus. I also wish to express my in-

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[17] Meyer, *Ber.*, 44,2718 (1911): ibid., 45, 2843 (1912).

debtedness to Professor N. Bjerrum, whose many valuable suggestions have been of great importance to my work, and to Mr. E. A. Guggenheim for helpful criticism.

Summary

1. The kinetics of the ketonic decomposition of α,α-dimethylacetoacetic acid, $CH_3COC(CH_3)_2COOH \longrightarrow CH_3COCH(CH_3)_2 + CO_2$, have been studied. Experiments were made in hydrochloric acid, glycolate and acetate buffers.
2. The dissociation constant of α,α-dimethylacetoacetic acid has been calculated from the experimental results.
3. It has been shown that the decomposition is catalyzed by amines.
4. From the fact that α,α-dimethylacetoacetic acid is unstable it follows that the keto form of β-keto carboxylic acids is unstable.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF BRITISH COLUMBIA]

EXTRACTION OF COMMERCIAL RARE-EARTH RESIDUES WITH A VIEW TO THE CONCENTRATION OF ILLINIUM

BY ROBERT W. BALL[1] WITH J. ALLEN HARRIS[2]

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Historical

In 1926[3] one of the writers, in conjunction with Professor B. S. Hopkins of the University of Illinois, was able to isolate, although in an impure state, sufficient of Element 61 to be able to identify it by means of x-ray analyses. Since, however, some 700 pounds of original material yielded a concentrate of but a few grams, it would seem to indicate that (a) the element is extremely rare and hence, in order to obtain quantities sufficiently great for purification, enormous amounts of the original material must be worked on, or (b) that while not rare, our method of concentration was inefficient and considerable of the element was lost at different stages of the treatment involved.

Assuming the latter possibility, one of the most likely sources of loss would be inefficiency in extraction of original residues; this possibility is discussed in this paper.

The element has not yet been obtained in a state of purity great enough to permit the mapping of its arc and absorption spectra, so it is impossible

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[1] Part of this paper was presented as a thesis for the M.A. degree at the University of British Columbia.

[2] National Research Fellow. Paper completed at the Sorbonne, Paris, as part of work under National Research Council Award.

[3] Harris with Hopkins, THIS JOURNAL, 48, 1585 (1926).

to make use of these in following the progress of concentration. Similarly, x-ray analyses are not sensitive when amounts of less than one part per thousand are present. Hence it was decided that the best method for attacking this problem would be from the standpoint of the quantitative determination of total rare-earth content of the original material, by analytical methods.

Introduction

The materials used in the investigation were (1) commercial double sulfates, having the same source as those used in the original concentration of illinium, and (2) commercial hydrated oxides, prepared by the Welsbach Company for the University of Illinois, and kindly loaned to us by Professor Hopkins.

However, although much work has been carried out regarding the extraction of the rare-earth minerals, and several methods have been devised for decomposing the double sulfates, it is probable that all of these methods are selective in their action and it does not appear that a single one of the methods has been studied from a quantitative view-point.

Analysis

Extremely careful analyses were made of the original materials, first by the method outlined by Hillebrand[4] and, second, by a modification of the above method which appeared to give results consistently concordant with the Hillebrand procedure.

The average of these analyses is: (1) double sulfates? 39.40 g. of rare earth as oxide per 100 g. of material; (2) hydrated oxides, 73.05 g. of rare earth as oxide per 100 g. of material.

Part I. Extraction of Double Sulfates

(a) Wet Extraction of Small Amounts.—Two-gram samples of the carefully dried material were moistened with water and then digested with **25** cc. of concd. nitric, hydrochloric and sulfuric acids, respectively, until the volume was reduced to about **5** cc. These were then taken up in **250** cc. of water and, after filtering, the residue was again treated with hot water, filtered and the filtrates combined. After correcting acidity to reduce solubility of the oxalates to a minimum,[5] the rare earths were precipitated as the oxalates, washed, dried and ignited to the oxides. The maximum and minimum of the results, which were never concordant, are as follows

Acid	Nitric	Hydrochloric	Sulfuric
Maximum yield as oxide, %	**15.73**	**29.07**	**39.87**
Minimum yield as oxide, %	**11.26**	**25.35**	**34.35**

These compared to actual content of **39.40%** as oxide indicated that concentrated sulfuric acid is the most efficient of the acids. Although the maximum value is more than the theoretical, the majority of extractions were in the vicinity of **39.0%.**

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[4] Hillebrand, U. S. Geological Survey Bulletin 700.

[5] Sarver and Brinton, THIS JOURNAL, **49,943** (1927); Neckers with Kremers, *ibid.*, **50, 950 (1928).**

Turning now to alkali extraction, the one recommended, as mentioned previously, is the use of a 50% solution of sodium hydroxide.

Accordingly, two-gram samples were digested for several hours with such a solution. The resulting mixture was taken up in 250 cc. of water and washed by decantation until alkali free; the residue was then digested with nitric acid to dissolve the hydroxides, diluted, filtered and the residue leached with hot water. The combined filtrates were subsequently treated with oxalic acid and the resulting oxalates ignited and weighed as the oxide. In all cases where there was evidence of a basic salt forming, the sample was rejected; maximum yield as oxide, 38.89%; minimum yield as oxide, 37.98%. Thus it may be seen that the alkali extraction gives more consistent results than does the extraction with acids.

(b) Fusion of Small Amounts.—The fluxes chosen were sodium hydroxide and sodium carbonate and the acids used as extractants of the melt were dilute and concentrated hydrochloric, nitric and sulfuric acids.

As in the previous cases, samples of two grams each were used and fused with excess of the flux. After lixiviating with water, the mass was extracted with acid of varying concentration. In the case of the dilute acids the results were never concordant; this no doubt was due to the tendency of the cerium to become basic. The best results were obtained by fuming the melt with concentrated sulfuric acid, and then extracting several times with hot water.

Flux	Sodium hydroxide	Sodium carbonate
Extractant	Concd. sulfuric acid	Concd. sulfuric acid
Rare earth as oxide, %	Av. 39.06	Av. 39.32
Total rare-earth content, 39.40		

In the foregoing determinations, then, it would appear as though extraction by means of sulfuric acid, sodium hydroxide or fusion with sodium hydroxide or sodium carbonate would eliminate possibility of loss of illinium during the initial extractions.

Since, however, the rare-earth worker is usually interested in larger amounts, it was deemed advisable to investigate the efficiency of these reagents on larger amounts of original material, up to 3000 g.

(a) Wet Extractions of Larger Amounts. (1) With Acids.—These gave results too low and so inconsistent as to render their use valueless.

(2) With 50% Sodium Hydroxide Solution.—This method, while giving excellent results on small samples, for larger amounts of material gave a maximum yield of but 18.34% as oxide against the actual content of 39.4%.

(3) Concentrated Sodium Hydroxide Solution.—The method suggested by Professor Urbain and the one used in his laboratory for decomposition of sulfates is a digestion with a saturated solution of sodium hydroxide. Two digestions with this solution gave the following results for amounts in the vicinity of 300 grams: A. % as oxide, 38.88—98.68% efficient; B. % as oxide, 39.20—99.49% efficient.

(4) Digestion with saturated Na_2CO_3 solution.—A. % as oxide, 34.82—88.37% efficient; B. % as oxide, 35.30—89.59% efficient. Hence for wet extractions a concentrated solution of sodium hydroxide is extremely efficient.

(b) Fusion with Sodium Carbonate.—These fusions were carried out in fire-clay crucibles in a gas-fired muffle furnace. Amounts of the commercial double sulfates in the vicinity of one kilogram were mixed with excess of dry sodium carbonate and fused until the mass was thoroughly molten. The temperature was then maintained for about an hour, the furnace allowed to cool and the crucible removed. Great difficulty was experienced in removing the melt from the container—the crucible usually had to be broken. The mass was then extracted and treated as in the case of the small samples. The maximum yield obtained by this method was 37.26 g. of oxide per one hundred grams of original material.

Believing the discrepancy to be due to incomplete removal of the melt from the crucible, a method was devised which is outlined below and which we cannot recommend too highly for large-scale laboratory operations. In addition to being highly efficient, it has the advantage of being a practically continuous process.

TABLE I

RESULTS OBTAINED BY THIS PROCESS

Original residue, g.	872.00	1000.00	1500.00	2000.00	3000.00
Oxides, g.	324.8	392.73	587.40	774.00	1169.99
Oxide per 100 g., g.	37.75	39.27	39.16	38.70	39.00
Efficiency, %	95.81	99.66	99.39	98.22	99.00

In the first and fourth cases the results are low—no doubt due to the fact that in both instances new crucibles were used and hence some of the melt was retained as a glaze during pouring. The last two fusions were carried out as a continuous process to test its possibilities.

Conclusions

The following methods are recommended as being efficient in extracting the rare earths from double sulfate residues.

(1) For Large Amounts.—The dried double sulfates are thoroughly mixed with a large excess of dry commercial sodium carbonate. The mixture is then fired in a muffle until molten and the temperature maintained until reaction is complete. The crucibles are then removed and the molten contents poured into a vessel containing hot water; the still red-hot crucible is quickly recharged and returned to the muffle. The sudden cooling of the melt causes thorough disintegration. When the last pouring has been made the crucibles are cooled somewhat and the addition of dilute sulfuric acid to the container effectively loosens all adhering melt, which may then be added to the solution.

The mixture is allowed to settle and the residue washed thoroughly by decantation until alkali-free. It is then transferred to a large evaporating dish and evaporated to dryness.

The dry residue is now made up to a thin paste with concentrated sulfuric acid and evaporated until there is copious evolution of fumes, in order to convert the rare earths into the soluble acid sulfates. The resulting mass is extracted with water until the last extraction gives no test for the rare earths.

These extracts are combined, diluted and the rare-earth hydroxides precipitated with ammonia, washed thoroughly to remove any sulfate, taken up in as little nitric acid as possible, diluted and precipitated as the oxalates with subsequent ignition to the oxide.

(2) **For Smaller** Amounts.—For amounts below one kilogram the following method is perhaps more adaptable. Moisten the dried residues with as little water as possible and cover with a saturated solution of sodium hydroxide to a depth of at least one inch. Digest on a steam-bath, following by digestion on a hot-plate until the mass is thoroughly disintegrated and the rare earths converted. to the bulky hydroxides. The mass is allowed to cool and any liquor is decanted. The hydroxides are then boiled with water until all alkali has been removed and extracted with dilute nitric acid, heating only sufficiently to aid the solution of the soluble portion. The undissolved residue is filtered off and extracted a second time. The filtrates containing the rare earths as nitrates are combined, precipitated by means of ammonia and after thorough washing treated as formerly.

Either of these methods will reduce to a minimum the possibility of loss of any rare earths and consequently illinium during the extraction of commercial double sulfates and will also yield a product of considerable purity.

Part II. Extraction of Commercial Hydrated Oxides

(a) Acid Extraction.—It is natural to assume that acid extractions of such residues would be the more efficient; consequently alkaline extractions were not used.

In the case of larger amounts, varying between 200 and **312** g., the maximum yields obtained from a great many extractions, covering both digestions with acid and addition of the material to the hot acid with constant stirring, were as follows

Extractant	**Hydrochloric acid**	**Sulfuric acid**	**Nitric acid**
Oxide per 100 g., g.	**60.19**	**70.36**	**68.40**

In all cases the tendency to become basic was very pronounced and had to be carefully guarded against. The best results are obtained by carefully moistening the original material with water, care being necessary as a great deal of heat is liberated. The material is then slaked with water and when concentrated nitric acid is slowly added complete solution takes place. The yield, however, is always low, but if a little hydrogen peroxide is added at this point the results are always concordant and **much** higher.

TABLE II

RESULTS BY THIS METHOD

Original material, g.	**200**	**200**
Oxides, g.	**145.82**	**144.70**
Wt. per 100 g., g.	**72.91**	**72.36**
Efficiency, %	**99.80**	**99.04**

Deep appreciation is hereby expressed to Professor Hopkins for the loan of material for the investigation; to the National Research Council and International Education Board for furnishing funds to allow a continuation of this work in Europe, and also to Professor Georges Urbain of the Sorbonne whose kindly advice and interest was a source of inspiration at all times.

Summary

1. As mentioned in the historical part of this paper, it was feared that there was a possibility of loss of illinium during original extraction of double sulfate residues. As the material used had been extracted with a 50% solution of sodium hydroxide, the foregoing experiments show that there is a possibility of loss of rare earths at this point.

2. A method has been outlined whereby using a sodium hydroxide solution, practically theoretical results—as compared with an accurate quantitative determination—have been obtained for amounts up to 300 g.

3. An equally efficient method for larger amounts, involving fusion with sodium carbonate, has been described.

4. The use of nitric acid and hydrogen peroxide is recommended for the extraction of commercial hydrated oxides. Hence, if the original material is extracted by any of the above methods, all of the rare earths, including illinium, should be found in the extract. All undissolved residues are, however, being investigated.

VANCOUVER, B. C.

[CONTRIBUTION FROM THE BIOCHEMIC DIVISION, BUREAU OF ANIMAL INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

DICHLORO-AMINE

BY ROBERT M. CHAPIN

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Available evidence for the existence of dichloro-amine, $NHCl_2$, including the most recent,[1] rests upon incidental observations made in the course of work on nitrogen trichloride. The conditions necessary for the formation of the substance remain undefined, while methods for its separation from the two other reaction products are lacking.

The nature of the product obtained through chlorination of an excess of ammonium ions is known to depend upon the reaction of the solution, acidity leading toward nitrogen trichloride and alkalinity toward monochloro-amine. It will be shown here that when the reaction is effected through rapid mixing of sufficiently cool and dilute buffered solutions, with ammonium ions always in excess, the nature of the product is governed solely by the concentration of hydrogen ions. In solutions more alkaline

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[1] W. A. Noyes, THIS JOURNAL, 42,2173 (1920).

than slightly above PH 8.5 nothing but monochloro-amine was found; below *P*H 4.4 nitrogen trichloride is produced with only a trace of chloro-amine; between PH 4.4 and 8.5 graduated mixtures of the two chloro-amines result. That is, while the shift between nitrogen trichloride and dichloro-amine is sharp near PH 4.4, there is a considerable range over which the two chloro-amines coexist in a ratio ultimately fixed by the hydrogen-ion concentration. Accordingly an acidified solution of monochloro-amine becomes proportionately converted to dichloro-amine on storage.

In the physical properties of odor, volatility from aqueous solution and relative solubility in various immiscible solvents, dichloro-amine is intermediate between nitrogen trichloride and monochloro-amine. Like these two it liberates iodine from an acidified solution of potassium iodide, and may be thus determined when free from both of the others. Removal of contaminating nitrogen trichloride is easily effected with little loss of chloro-amine by shaking out the aqueous solution with successive small proportions of carbon tetrachloride, but no way for removing contaminating monochloro-amine was found other than conversion to dichloro-amine by subjection to a sufficiently low hydrogen-ion concentration.

Mixtures of the two chloro-amines that are free from nitrogen trichloride may be assayed by determining the apparent partition ratio in an appropriate immiscible solvent, either chloroform, carbon tetrachloride or pure ether, and comparing the result with the partition ratios of the two pure substances in that solvent.

Experimental

The solutions of chlorine and of ammonium ions were mixed expeditiously and the products were stored in the dark at room temperature. The buffers employed in the preparations were acetate, phosphate or borate mixtures, which are resistant to chlorine. Hydrogen-ion concentrations were determined colorimetrically by standard methods (Clark) with the indicators methyl red, brom thymol blue, cresol red and thymol blue (alkaline range). Errors from bleaching could be sufficiently avoided by rapid work except that nitrogen trichloride required previous removal by carbon tetrachloride. Any solution to be analyzed for "available chlorine" was pipetted (tip beneath surface) into a flask already charged with a dilute iodine-free mixture of potassium iodide and the necessary excess of hydrochloric acid, with constant swirling. All extractions and subsequent analyses, once started, were put through as expeditiously as possible.

Experiment I.—The ammonium solution, 250 cc., was 0.1 M ammonium acetate brought to the desired *P*H by acid or alkali and in many cases carrying additional buffer. The chlorine solution, 250 cc., had been brought to the same *P*H by calculated addition of buffer to 100 cc. of chlorine water carrying 0.4 to 0.6% chlorine.

After admixture, storage and determination of the *P*H, the whole solution was thoroughly shaken with 10 cc. of carbon tetrachloride in a separatory funnel. A little of the carbon tetrachloride was discarded to rinse the stem of the funnel, then 5 cc. of the remainder was added to acidified potassium iodide'and titrated with 0.01 N sodium thiosulfate. After expulsion of sludge, extraction and titration were repeated until the slightness of the difference between successive results proved the absence of nitrogen trichloride.

Following extraction with carbon tetrachloride, the apparent partition ratio of the chloro-amine in chloroform was determined, 25 to 30 cc. of each liquid being thoroughly shaken together, and 20 cc. of each phase being titrated in acidified potassium iodide solution with 0.01 N thiosulfate. Many of these determinations were made in duplicate.

The results of Expt. 1 are contained in Table I. Owing to the formation of acid in the reaction, the final PH usually fell below the calculated initial PH to a degree dependent upon the nature and proportion of buffer present. There appears a marked difference in the solubility and hence in the nature, of the substances extracted by carbon tetrachloride from Preparations A and B, respectively. The partition ratio in chloroform of Preparation A was not determined because the total available chlorine remaining after the fourth carbon tetrachloride extraction required only **3.8** cc. of 0.01 N thiosulfate per 50 cc.

TABLE I

INFLUENCE OF HYDROGEN-ION CONCENTRATION UPON PRODUCTS IN EXPERIMENTS 1 AND 2

Expt.	Prep.	Init. *P*H, calcd.	Final *P*H, detd.	Time, hours	$Na_2S_2O_3$ titr. of CCl_4 extracts 1	2	3	Part. ratio, $\frac{CHCl_3}{aq.}$	$\frac{D\ c.a.\text{-}Cl}{Total\ c.a.\text{-}Cl}$, %
1	A	4.3	4.4	0.75	136.5	26.3	4.8[a]		
	B	4.6	4.4	.75	8.0	7.8	7.7	1.87	99.8
	C	7.0	5.5	1.25	5.9	5.7		1.63	92.9
	D	8.0	6.5	1.25	4.6	4.3		0.99	
			6.4	21.5				.98	65.5
	E	8.0	7.0	3	1.85	1.75		.68	45.2
	F	8.0	7.3	1.5				.66	43.7
	G	8.0	8.0	1.25	1.35			.28	3 5
	H	8.4	8.5	0.75	0.9			.252	0.4
	I	9.2	8.9	.75	.9	0.9		.249	.0
		(detd.)							
2	A	4.2		20	12.4	2.15	0.7		
	B	4.6	4.4	21	6.6	6.4		1.90	100.0
	C	4.8	4.7	22	7.05	6.9		1.87	99.8
	D	4.9	4.8	18.5	6.25	6.05	5.95	1.86	99.5
	E	5.3	5.2	43	4.25	4.2		1.86	99.5
	F	5.5	5.3	44	3.8	3.75		1.84	99.0
	G	>9	>9	2				0.25	0.0

[a] Titration of fourth CCl_4 extract = 1.2 cc.

Experiment 2.—This experiment shows the effect of acidification upon monochloro-amine. The ammonium solution contained 30 cc. of 10% ammonium sulfate and 5 cc. of N sodium hydroxide in 200 cc. The chlorine solution contained 100 cc. of chlorine water and 20 cc. of *N* sodium hydroxide in 200 cc. After admixture and standing for one hour, a predetermined quantity of 0.5 N acetic acid was added and the PH was immediately determined. Other determinations were made after a further interval, as shown in Table I. As in Expt. 1, Preparations A and B on either side of PH 4.4 yielded different substances to extraction by carbon tetrachloride. It is also evident that monochloro-amine held at *PH* 4.4 to **5.3** undergoes extensive conversion to dichloro-amine.

Experiment 3.—The rate of the formation of dichloro-amine from chlorine and ammonium ions at a favorable *PH* was next investigated. Mixtures were made as in Expt. 1 at a calculated initial *PH* of 4.9. The results are contained in Table II. Residual Preparation B after standing for a total of three hours was extracted twice with carbon tetrachloride. The obtained titrations of 9.50 and 9.25 cc of **0** 01 N thiosulfate showed freedom from nitrogen trichloride. Accordingly, the reactions leading to dichloro-amine under the most favorable conditions require at least one to two hours for completion.

TABLE II

INFLUENCE OF TIME UPON FORMATION OF DICHLORO-AMINE IN EXPERIMENT 3

			Partition in CCl_4			Partition in $CHCl_3$		
Prepn.	Time, min.	PH, detd.	CCl_4 phase; titrn.	Aq. phase; titn.	$\frac{CCl_4}{aq.}$	$CHCl_3$ phase; titrn.	Aq. phase; titrn.	$\frac{CHCl_3}{aq.}$
A	2		29.0	42.4	0.68			
	17		26.7	36.3	.74			
	60	4.7	26.0	32.8	.79			
	120		24.3	30.1	.81			
B	15					47.2	26.3	1.79
	60		24.2	28.1	.86	44.6	23.7	1.88
	120	4.6	22.6	26.6	.85	44.0	23.7	1.86

Experiment 4.—Marckwald and Wille[2] found the partition ratio of monochloro-amine between ether and water to be near unity. To determine that of dichloro-amine, portions of Preparation B of Expt. **3** after the two extractions by carbon tetrachloride were shaken with ether, free from peroxide and alcohol, and the partition ratio was determined as before described, except that only 10 cc. of the ether layer was pipetted out, and this was discharged into 10 cc. of carbon tetrachloride underlying the acidified potassium iodide in the flask in order to sink the non-aqueous solvent. Two trials gave partition ratios of **47.5** and **47.0.**

On the assumption that dichloro-amine was the sole product present at *a PH* slightly above *4.4,* the previous experiments indicate the following partition ratios

Monochloro-amine in chloroform	0.25
Dichloro-amine in chloroform	1.88
Dichloro-amine in carbon tetrachloride	0.85
Dichloro-amine in ether	47.3

From the partition ratios of the two pure chloro-amines in chloroform, the percentage of dichloro-amine chlorine in total chloro-amine chlorine

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[2] Marckwald and Wille, Ber., 56, 1319 (1923).

may accordingly be calculated from the apparent partition ratio, R, of a mixture by the formula

$$44.2 = \frac{4R - 1}{R + 1}$$

Application of this formula gave the results in the last column of Table I.

Experiment 5.—With respect to the determination of the chlorine–nitrogen ratio in the supposed dichloro-amine, the work of Noyes[1] on nitrogen trichloride indicated that transfer of the substance to an immiscible solvent would be the best means for purification from ammonium salts and chloride. For the actual analysis the methods of Marckwald and Wille[2] for monochloro-amine were followed as closely as possible.

Preparations were made as in Expt. 1 but with the chlorine water increased to 150 or 200 cc. After one hour the PH was found to lie between 4.5 and 4.7 and freedom from nitrogen trichloride was proved by two extractions with carbon tetrachloride. Dichloro-amine was then extracted with 125 cc. of peroxide-free ether. The ether extract was transferred to a small separatory funnel and washed four times with 10 to 15 cc. of acetate buffer of PH 4.5, though the last wash was not removed. The second and third washings afforded only opalescences with silver nitrate solution.

From the clear ether layer 50 cc. was pipetted into a 200-cc. volumetric flask containing 35 to 50 cc. of strong aqueous sulfur dioxide, while 10 cc. was pipetted into a glass-stoppered flask charged with acidified potassium iodide and 10 cc. of carbon tetrachloride. The liberated iodine in the latter flask was at once titrated with 0.1 N sodium thiosulfate.

The flask containing sulfur dioxide and ethereal solution was stoppered and frequently shaken for one-half hour; then the ether and evident excess of sulfur dioxide were gently boiled off. Half of the cooled solution was taken for cold precipitation of silver chloride and half for distillation of ammonia into 0.1 N acid. The results in Table III appear adequate to identify the substance as well as to prove the applicability of the assay method for "available chlorine."

TABLE III

ANALYTICAL RESULTS ON DICHLORO-AMINE SOLUTIONS IN EXPT. 5

				Results in g. per 100 cc.			
Prepn.	$Na_2S_2O_3$, titrn.	AgCl, g.	NH_3, titrn.	"Avail. Cl"/2	Total Cl	N	At. ratio, total Cl/N
A	16.19	0.2945	10.10	0.2870	0.2914	0.0566	2.034
B	12.09	.2147	7.50	.2144	.2125	.0420	1.998

Experiments on the germicidal powers of dichloro-amine have been begun in these Laboratories.

Summary

Dichloro-amine is produced by chlorination of excess ammonium ions at PH 4.4 to 8.5, being practically the sole ultimate product at PH 4.5 to

5.0, and, likewise, by corresponding acidification of monochloro-amine solutions. It was identified through its behavior with immiscible solvents and by its chlorine–nitrogen ratio.

WASHINGTON, D. C.

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

THE DETERMINATION OF FERROUS IRON IN SILICATE ROCKS. II. ELECTROMETRIC

BY BYRON A. SOULE

RECEIVED MARCH 30, 1929 PUBLISHED JULY 5, 1929

In a previous article[1] it was shown that the ferrous iron content of silicate rocks can be determined by decomposing the sample with hydrofluoric acid in a pyrex glass flask, diluting with a solution of boric acid and titrating with standardized potassium permanganate. The method has two advantages over that commonly used: (a) the course of decomposition can be watched, and (b) solution and titration are conducted in the same vessel. The most significant disadvantage is that a correction must be applied for the permanganate reduced by dissolved glass constituents.

A consideration of the composition of pyrex glass[2] suggested that arsenic might be the only disturbing element. It was therefore decided to try ceric sulfate as the oxidizing agent, Willard and Young[3] having reported that the titration is not affected by a moderate amount of arsenious acid. The results obtained were satisfactory and led to the development of the method herein advocated.

Materials

Apparatus.—The decomposition flasks were of two sorts: (1) ordinary 250-cc. pyrex glass suction flasks, each having an especially made, well fitting, glass stopper provided with an outlet tube 1 cm. in diameter and bent sharply at the lower end to almost touch the side of the flask; (2) 250-cc. transparent, fused quartz, Erlenmeyer flasks with similar stoppers.

Titrations were conducted with the aid of a bimetallic electrode system similar to that suggested by Furman and Wilson.[4] The resistance used was 240,000 ohms. The electrodes were prepared from pieces of No. 27 B. and S. gage platinum wire and silver wire[5] annealed at 100–105°, then sealed into the ends of glass tubes as usual. About 3 cm. of the platinum and 6 cm. of the silver wire projected. When not in use the anode was kept in a solution of ceric sulfate and the cathode in dilute ammonia water.

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[1] Soule, THIS JOURNAL, 50, 1691 (1928).

[2] U. S. Bureau of Standards Tech. Paper 107, p. 8.

[3] Willard and Young, THIS JOURNAL, 50, 1335 (1928).

[4] Furman and Wilson, *ibid.*, 50, 277 (1928).

[5] This work was nearing completion when the article by Brann and Clapp, *ibid.*, 51, 39 (1929), appeared.

Reagents

The ceric sulfate solution was prepared from U. S. P. quality cerium oxalate by a method similar to that of Willard and Young.[6]

The electrolytic iron, especially prepared and carefully preserved under hydrogen in the form of cubes weighing approximately 0.1 g., had been analyzed by several workers and found to contain impurities totaling not over 0.03%.

Carbon dioxide was obtained from a commercial cylinder and passed through chromous chloride to remove any oxygen.[7] The purified gas was tested and found satisfactory.

Water for standard solutions was redistilled first from alkaline permanganate then from sulfuric acid. Just before use all water was boiled and cooled.

All other reagents were carefully tested in order to prove that they would introduce no error.

Weighings.—Standard solutions were weighed directly. All other weighings were by substitution.

Experimental

Standardization of Ceric Sulfate.—A single cube of electrolytic iron was placed in a glass flask filled with carbon dioxide; 10 cc. of sulfuric acid (1 :6) was added and the flask gently warmed. After fifteen to twenty minutes, when the iron had dissolved, the rate of flow of carbon dioxide was increased. Then 100 cc. of water containing 5 g. of boric acid and 5 cc. of hydrofluoric acid (48%) was added, with care that no air should be drawn in during the operation. After the addition of a few drops of concentrated hydrochloric acid the mixture was titrated electrometrically with ceric sulfate.

Four consecutive determinations gave an average iron equivalence of 0.0034685 g. of iron per gram of solution, that is, a normality of 0.04828.

Determination of Ferrous Iron in Magnetite.[8,9]—A 0.3–0.4 g. sample of magnetite[10] was placed in a glass flask filled with carbon dioxide. Next

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[6] Willard and Young, THIS JOURNAL, 50, 1322 (1928); 51, 149 (1929).

[7] Moser, *Z. anorg. Chem.*, *110*, 126 (1920).

[8] U. S. Bureau of Standards, Sample No. 29, even though it contains but 12.02% of SiO_2, was selected to illustrate the method proposed because of its status. The FeO content is 24.78% according to the certificate, dated Dec. 1, 1910. This value, apparently contrary to the present practice of the Bureau, is the work of but one analyst, which point together with the early date should be taken into consideration when comparing the figure with averages here reported.

[9] Compare Adam, *J. S. African Chem. Inst.*, *8*, 7 (1925). A copy of this article was obtained after the work here reported had been finished. In agreement with Adam it should be emphasized that HCl + HF + water as a solvent was found far more satisfactory than H_2SO_4 + HF + water, especially, for magnetites. Ores that were dissolved only after long and repeated boiling in the latter mixture were completely decomposed by the former in less than five minutes at a temperature approximating 50°. Combinations of sulfuric acid and hydrochloric acid in various ratios were distinctly less efficient than hydrochloric acid alone.

[10] See U. S. Bureau of Standards Circular No. 26, p. 4, for procedure when drying sample.

10 cc. of hydrochloric acid (35%) and 3 cc. of hydrofluoric acid (48%) were added and the flask gently warmed (40–50°) until no black residue was discernible. This required three to five minutes. Then the rate of flow of carbon dioxide was increased and 100 cc. of water containing 5 g. of boric acid and 5 cc. of sulfuric acid (1:6) was added. The mixture was titrated immediately. Results obtained on three consecutive days are given in Table I.

TABLE I

DETERMINATION OF FEO IN BUREAU OF STANDARDS MAGNETITE (IRON ORE NO. 29)

1 g. of $Ce(SO_4)_2$ soln. $\approx$ 0.0034685 g. FeO. Certificate value of FeO in Fe_3O_4 = 24.78%

	Fe_3O_4, g.	$Ce(SO_4)_2$ soln., g.	FeO, %	
1	0.2776	19.635	24.53	Average, 24.57
	.2806	19.900	24.58	
	.3012	21.355	24.59	
2	.3793	26.832	24.54	Average, 24.56
	.4019	28.445	24.55	
	.3192	22.649	24.60	
	.3852	27.229	24.52	
	.4206	29.824	24.60	
3	.4609	32.613	24.54	Average, 24.54
	.4077	28.859	24.55	
	.3683	26.038	24.52	

Restandardization of Ceric Sulfate.—On the same day that the third set of magnetite samples was analyzed the ceric sulfate was again standardized against electrolytic iron using essentially the method originally employed. The average of results obtained was 0.04827 N by weight. The solution was then compared with a different primary standard, retaining, in so far as possible, a final reaction essentially similar to that originally used. The three steps following were completed in one day.

First, 0.1 N potassium permanganate was standardized against Bureau of Standards sodium oxalate.[11] Next, portions of a sample of ferrous sulfate, selected and tested for uniformity of composition, were transferred to 500-cc. Erlenmeyer flasks filled with carbon dioxide; 200 cc. of water and 10 cc. of sulfuric acid (1:1) were added and the solution was titrated at once with the permanganate just standardized. Determining the equivalence point visually the average of three consecutive results, expressed in ferrous iron content, was 26.63% of FeO. Finally, the ferrous sulfate was titrated with ceric sulfate, using the same reagents as for analysis of magnetite but modifying the procedure to the extent that the reagents were all added at once and the titration was carried out immediately. The average of three consecutive determinations showed an iron content of 26.60% of FeO. Later, the ferrous sulfate was

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[11] For details of procedure see the certificate or McBride, THIS JOURNAL, 34, 393 (1912).

again analyzed using exactly the same procedure as for magnetite. The results averaged 26.66% of FeO.

In order to detect any effect due to the decomposition flask, samples of magnetite were analyzed by the usual procedure in flasks of transparent fused quartz. The average of three consecutive results was 24.58% of FeO.

As a final variation a silver chloride electrode[12] was substituted for the silver wire. Three more analyses of magnetite gave an average of 24.55% of FeO.

Discussion

Among the sources of error encountered in the determination of ferrous iron those leading to low results are considered to be the more common. In the work under consideration thorough preliminary tests and the experiments with ferrous sulfate would indicate that the reagents were satisfactory and the measures for protecting against atmospheric oxidation adequate. The question of low results due to the current generated during titration by the method of Furman and Wilson can be dismissed after a brief calculation. Assuming a titration period double that required and the maximum instead of the average galvanometer deflection only 1.5×10^{-6} g. of FeO would be oxidized.

Another source of error mentioned especially by Adam[g] is "whether the HCl decomposition takes place without oxidation of a part of the ferrous iron." In the preliminary work experiments were conducted involving variations in amount of hydrochloric acid up to 25 cc. and time of digestion up to 160 minutes. No effect attributable to such variations was found.

Summary

Ferrous iron can be determined quickly and accurately in magnetites and materials of higher silicate content by electrometric titration with ceric sulfate after decomposition in a pyrex glass flask by a mixture of hydrochloric and hydrofluoric acids. Reducing agents derived from the glass have no effect.

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[12] Willard and Fenwick, THIS JOURNAL, 44,2508 (1922).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 223]

CHEMICAL REACTIONS OF DRIED SUBSTANCES. I. AMMONIA AND PHOSPHORUS PENTOXIDE

BY LOUIS HARRIS AND CHARLES BUSHNELL WOOSTER[1]

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It was reported by H. B. Baker[2] that phosphorus pentoxide did not absorb thoroughly dried ammonia. Gutmann[3] was unable to duplicate these results but he failed to describe the purity of the phosphorus pentoxide and the method of introducing it into his apparatus. Baker[4] repeated his own experiments and reaffirmed his claim, suggesting that the presence of metaphosphoric acid would explain the absorption of ammonia observed by Gutmann. Recently, Robertson, Fox and Hiscocks[5] passed dried and purified ammonia through a tube of phosphorus pentoxide and confined it over mercury in contact with the pentoxide. They observed a slight reaction at first, after which no decrease in volume occurred during forty-eight hours.

In several of these investigations the experimental conditions were such that the ammonia might have partly saturated the phosphorus pentoxide before the observations were made. Furthermore, the possible formation of a protective film upon the pentoxide was not excluded. It appeared worth while, therefore, to repeat the experiments, avoiding these sources of uncertainty and taking the additional precautions made possible by modern, high-vacuum technique. The hazard of preliminary saturation of the phosphorus pentoxide may be eliminated by observing the pressure of ammonia before as well as after exposure to it and the possibility of film formation may be tested by exposing the gas to a fresh surface of the pentoxide after reaction with the first sample has ceased.

Baker dried his apparatus by heating the glass nearly to the softening point and simultaneously drawing through it a stream of air dried with sulfuric acid. Ammonia was prepared from ammonium chloride and dried over lime for several days. A thin glass tube containing sublimed phosphorus pentoxide was broken in a reaction chamber containing the dried ammonia and pressure changes were observed on a mercury manometer.

In the present investigation it was considered desirable to dry the apparatus by evacuation at elevated temperatures, to employ phosphorus

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[1] National Research Fellow.

[2] Baker, *J. Chem. Soc.*, 65, **611** (1894).

[3] Gutmann, *Ann.*, **299**, 273 (1898).

[4] Baker, *J. Chem. Soc.*, **73**, 422 (1898).

[5] Robertson, Fox and Hiscocks, "Studies in the Infra Red Region of the Spectrum, II," *Proc. Roy. Soc. London*, **120**, 157 (1928).

pentoxide free from lower oxides[6] and observable quantities of metaphosphoric acid and to use ammonia which, after drying with dissolved sodium, had been triply distilled without further contact with any but dried and outgassed surfaces of pyrex glass and fused quartz.

Experimental Part

Apparatus.—The apparatus consisted essentially of purification trains for the reagents, a storage bulb for the ammonia and storage tubes for the phosphorus pentoxide, a quartz spiral manometer (connected by means of a graded seal) and suitable attachments for evacuating the system. A diagram appears in Fig. 1. The points at which various sections were sealed off during the manipulation are indicated by constrictions. Temporary separation of various parts was accomplished by the use of plunger stopcocks of the Richards type through which were made the connections described later.

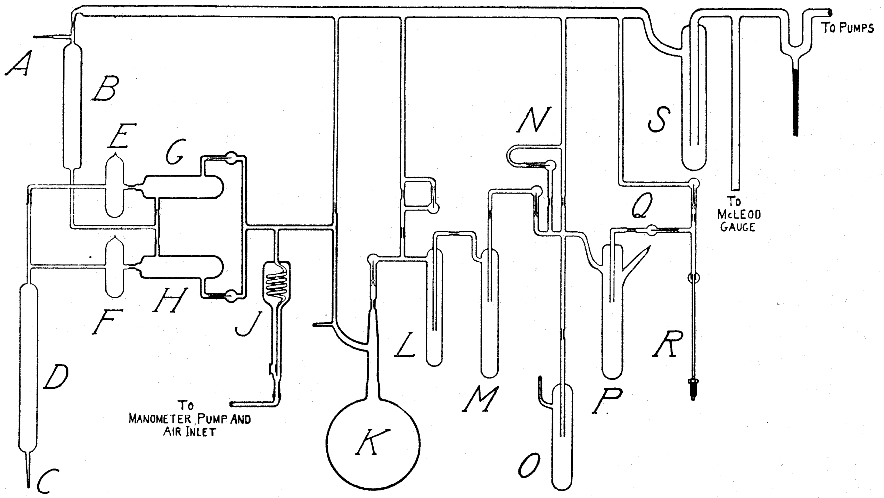

Fig. 1.—Apparatus for studying the reaction between dried ammonia and phosphorus pentoxide.

The iron cores were enclosed in glass sheaths to prevent contact between ammonia and the metal surfaces. A small mirror mounted on the indicator of the quartz manometer reflected the image of a straight filament upon a ground-glass scale placed at a distance of three meters. The manometer was used as a null instrument, balancing the pressures within it by external pressures which were read on a mercury manometer. Readings were accurate and reproducible to one millimeter. This auxiliary equipment is not shown in the diagram.

Method of Drying.—The glass and quartz surfaces were outgassed by evacuating through a liquid-air trap S with a mercury diffusion pump and a high-vacuum type of oil pump fifteen hours a day for five days. During this pumping the apparatus was intermittently heated with a blow torch until a yellow color was imparted to the flame and a high-tension discharge from a high frequency coil (which gives a one-inch spark in air) played upon the hot surfaces. After the third day no discharge from the heated

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[6] Biltz, *Ber.*, 27, 1257 (1894), observed that the presence of lower oxides caused absorption of the ammonia.

surfaces was observable. At the end of the five-day period the pumps could be disconnected for nine hours without a rise in pressure of more than 3 × 10^{-6} mm. of mercury. The direct leads to the pumps were then sealed off.

Materials.—Several brands of C. P. phosphorus pentoxide were tested for lower oxides and organic matter. The tests used for lower oxides were the mercuric chloride test advocated by Whittaker[7] and the silver nitrate test suggested by Finch and Peto[8] which is claimed to be the more sensitive by Finch and Fraser.[9] Our observations confirm this claim. One brand which was nearly free from these impurities was selected and further purified by sublimation at 800° in a stream of oxygen according to the directions of Finch and Fraser[9] and obtained in the highly pure and voluminous form which they described. Samples of this purified material were placed in the sublimation tubes E, F which were sealed off and evacuated. The surfaces of the storage tubes G, H were then outgassed and dried as described. The fine capillary C which terminated the inlet was broken and a stream of dry air entered through the phosphorus pentoxide protection tube D. The tip A of the second protection tube B was broken to provide an outlet and a slow stream of oxygen, dried by passage through an additional phosphorus pentoxide tube 80 cm. in length, was led through the sublimation train. Upon moderate heating, the pentoxide in the sublimation tubes readily sublimed and collected in the storage tubes as a voluminous deposit of feathery crystals and white powder. This material was apparently free from metaphosphoric acid, since it could be sublimed from one part of the tube to another without leaving any visible residue. The sublimation tubes together with the attached guard tube D were sealed off, the tip A of the second guard tube sealed and the storage tubes evacuated. Thus the storage tubes were protected by a guard tube of phosphorus pentoxide and a liquid-air trap. They were heated as hot as possible without driving out the pentoxide and treated with the discharge until a satisfactory vacuum and outgassing had been achieved, when they were sealed off from the vacuum line. Samples of the material which had collected in the connecting tubes were tested and found to be free from lower oxides.

Commercial anhydrous liquid ammonia was used as a starting material. This had been in contact with sodium in a special steel cylinder for four months. The outlet R of this cylinder was attached to the purification train with de Khotinsky cement. The connecting tubes between the tank and the first stopcock Q were pumped out but could not be heated, so the entering ammonia was redried by condensation at −78° into the first distillation tube, P, which contained metallic sodium. As soon as a sufficient quantity had collected, the lead from the tank was sealed off and the solution of sodium in the liquid ammonia allowed to stand for five hours.

One-third of the ammonia was distilled into a receiver O and discarded after sealing off this receiver. Baths of solid carbon dioxide in alcohol were used as refrigerants in all of the distillations. Hydrogen present in the vapors was now removed by connecting the first distillation tube through a stopcock N to the vacuum pumps. The ammonia was kept at −78° during this process and after the pumping was completed the vacuum connection was sealed off. Connection was then made to the second distillation tube M, one-half of the remaining ammonia distilled into it and this sample twice fractionated, retaining only the middle third at each step. Economy of apparatus and manipulation was achieved by returning the first third of each distillate to the residue and discarding them together.

Before allowing a sample to evaporate from the third distillation tube L into the storage bulb K, connection was made to the vacuum pumps for a short time to ensure

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[7] Whittaker, J. Chem. *Soc.*, **127, 2221 (1925).**

[8] Finch and Peto, *ibid.*, **121,692 (1922).**

[9] Finch and Fraser, *ibid.*, **129, 117 (1926).**

complete removal of any residual traces of hydrogen. When the vacuum connection had been sealed off and the stopcock leading to the storage bulb opened, a deflection of the quartz manometer J was observed which was found to indicate a pressure of 46.0 mm. (of mercury) within the system. As the ammonia in the third tube was partly frozen to a white solid at this time, this value should correspond to the vapor pressure at the melting point. This pressure is given by Landolt-Börnstein[10] as 44.9 mm., thus providing a check upon the reliability of the manometer. The purified ammonia was allowed to evaporate until the storage bulb was filled to a pressure slightly below atmospheric when the third distillation tube and the stopcock were sealed off.

The Action of Dried Ammonia on Phosphorus Pentoxide.—The volume of the storage bulb, manometer and connecting tubes had been found to be 1124 cc. by allowing dried air to expand into this system from a bulb of known volume. Accordingly, by reading the pressure and noting the temperature of a water-bath surrounding the storage bulb, the amount of ammonia therein (0.742 g.) could be determined. The volumes of the two phosphorus pentoxide storage tubes (neglecting the volume of the pentoxide, itself) was also known and thus the drop in pressure, due to expansion alone, upon connecting these tubes with the bulb could be calculated.

When the stopcock leading to the first pentoxide tube was opened a very rapid drop in pressure occurred which only continued for less than one minute. Thereafter the pressure fell very slowly. During the reaction some of the pentoxide near the ammonia entrance shrank considerably in volume and took on a glassy appearance. In other parts of the tube its appearance was not so markedly changed. Since the tube became heated during the reaction, one hour and fifteen minutes was allowed for cooling and the pressure then determined. Upon standing thirteen hours the pressures dropped 7.4 mm. (of mercury) more. The second pentoxide tube was then connected and a similar effect was observed. The data for these pressure changes appear in Table I. The third column lists the pressures in mm. of mercury before opening the pentoxide tubes, the fourth the new pressures calculated for expansion only, the fifth the new pressures observed, the sixth the drop in pressure due to absorption.

TABLE I

PRESSURE CHANGES DURING RAPID REACTION

Tube no.	Volume, cc.	P_1	P_2 (calcd.)	P_2 (obs.)	P (abs)	Temp., °C.
I	52	713	682	532.5	149.5	21.3
II	47	525.1	505	122.9	382.1	20.3

The system was allowed to stand for two days after these observations were made and the pressure read from time to time. These values, corrected for temperature variations, together with the time intervals are given in Table II.

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[10] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Berlin, 1923, Vol. II, p. 1345.

TABLE II

PRESSURE CHANGES SUBSEQUENT TO RAPID REACTION

Pressure, mm.	122.8	119.8	113.9	102.8	92.0
Time, min.	0	85	320	1370	2810

The second pentoxide tube was then heated to 74° in a water-bath but no effect upon the pressure was observed beyond that calculated for expansion. This indicates the occurrence of a true reaction as opposed to mere adsorption.

Finally, dry air was admitted to the system and the two pentoxide tubes were sealed off. These were weighed, broken open, cleaned out with water and reweighed. By subtracting from the total weight of the contents of each tube the weight of ammonia absorbed in that tube as calculated from the pressure drop, the amount of pentoxide originally present was determined. These data appear in Table III, where Col. 2 gives the amounts of phosphorus pentoxide in each tube, Col. 3 the amount of ammonia actually absorbed and Cols. 4 and 5 give the amount calculated upon the assumption that one and two moles of ammonia, respectively, react per mole of pentoxide.

TABLE III

ABSORPTION OF AMMONIA BY PHOSPHORUS PENTOXIDE

Tube no.	P_2O_5, g.	NH_3(obs.), g.	NH_3 (calcd., 1 mole), g.	NH_3 (calcd., 2 moles), g.
I	3.060	0.162	0.366	0.732
II	5.635	.435	.673	1.346

It was noticed that, whereas part of the contents of the pentoxide tubes was glassy in appearance and dissolved but slowly in water, other portions reacted vigorously, indicating the presence of unused pentoxide. The aqueous solutions were tested and the absence of lower oxides in the reaction product was demonstrated.

Conclusions

There is, of course, no known method of establishing the precise degree of dryness actually attained in an investigation of the kind here described. It is the opinion of the authors, however, that the procedure employed was at least equal, and in some respects superior, to that described by the previous investigators.

It is a noteworthy fact that the amount of ammonia absorbed in the period of rapid reaction was insufficient to saturate the available phosphorus pentoxide. This is evident from Table III upon comparing the observed absorption with that calculated even upon the assumption that only one mole of ammonia reacts with one mole of the pentoxide. The actual difference is probably much greater, for the nature of the reaction products obtained by various investigators[11] indicates that at least *two* molecules of the gas are involved in the reaction. This marked retardation of the absorption cannot be ascribed to the removal of residual traces of moisture from the ammonia since a rapid absorption again took place when *a* fresh surface of the pentoxide was exposed. The effect may be explained by assuming the formation of a protective film of the reaction product upon the phosphorus pentoxide. This assumption is compatible with the appearance and character of the reaction product obtained.

No indications of such film formation have been reported by the previous workers and the information which they give is not sufficient to determine to what extent their observations may have been influenced by this effect.[12]

Summary

1. Pure phosphorus pentoxide has been found to absorb appreciable quantities of carefully dried ammonia rapidly.

2. Evidence has been obtained indicating that the reaction product forms a protective film upon the pentoxide which retards further absorption.

CAMBRIDGE, MASSACHUSETTS

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[11] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," London, 1928, Vol. VIII, pp. 708–711.

[12] After this paper was submitted for publication our attention was called to an article by H. Tramm [*Z. physik. Chem.*, **105**, 356 (1923)]. He found that phosphorus pentoxide reacted with ammonia dried by Baker's procedure or by dissolving sodium in the liquid ammonia. However, he reported that ammonia dried by passage over sodium wire and then through liquid sodium–potassium alloy did not react with the pentoxide. He did not consider the possible influence of the formation of a protective film upon the pentoxide and it appears from the description that the ammonia was first admitted at low pressure into the pentoxide tube. Under such conditions film formation might occur without a very noticeable heat effect and thus the disappearance of a small amount of ammonia at the beginning of the experiment might have been unnoticed. Since he did not state his criterion for reaction, it seems advisable to reserve judgment upon his experiment until it has been repeated.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

A STUDY OF THE PRODUCTS OBTAINED BY THE REDUCING ACTION OF METALS UPON SALTS IN LIQUID AMMONIA SOLUTION. I. INTRODUCTION. II. THE ACTION OF SODIUM UPON ZINC CYANIDE

BY WAYLAND M. BURGESS AND ARTHUR ROSE*

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I. Introduction

When an alkali metal is dissolved in liquid ammonia, it ionizes, forming cations identical with the positive ion of a salt of this metal, and anions consisting of solvated electrons.[2] This solution containing free electrons is a most powerful reducing agent. Many reactions between solutions of this kind and both organic and inorganic compounds have been carried out.[3] A quantitative method for analysis of chlorine in organic compounds has been developed in this way.[4] Many of the reactions, however, have been studied chiefly from a qualitative point of view. A quantitative investigation of reactions of this type and of the products formed is being carried out in this Laboratory. The present series of papers deals with the results obtained with inorganic salts.

The type reactions that may take place between ammonia solutions of the metals and salts have been presented by Kraus and Kurtz.[3j] With the alkali or alkaline earth metals and salts of less positive metals, reaction may occur in which the cation is reduced and precipitated as free metal, or is reduced further and forms a compound, usually insoluble, with the reducing metal. These possibilities were illustrated by Kraus and Kurtz[3j] with numerous reactions. In some cases compounds of unusual composition were postulated as, for example, $NaZn_4$, Ca_7Zn. These formulas were established only from the ratio of reacting materials, and not by analysis. It is the purpose of this investigation to isolate the products formed in reaction between salts and metal solutions, determine their composition by analysis and make a study of their properties.

II. The Action of Sodium upon Zinc Cyanide

Introduction.—Kraus and Kurtz[3j] found that sodium reacts very readily with zinc cyanide in liquid ammonia solution, forming a finely-

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[*] This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Arthur Rose in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Kraus, THIS JOURNAL, 30, 1323 (1908).

[3] (a) Joannis, *Compt. rend.*, 113, 795 (1891); (b) Moissan, *ibid.*, 136, 1217 (1903); (c) Lebeau, *ibid.*, 140, 1042, 1264 (1905); (d) Chablay, *ibid.*, 140, 1262 (1905); (e) 154, 364 (1912); (f) Peck, THIS JOURNAL, 40, 335 (1918); (g) Kraus and White, *ibid.*, 45, 768 (1923); (h) White, *ibid.*, 45, 779, 1780 (1923); (i) Bergstrom, *ibid.*, 45, 2788 (1923); (j) Kraus and Kurtz, *ibid.*, **47, 43** (1925); and others.

[4] Chablay, *Ann. chim.*, [9] 1, 469 (1914); Clifford, THIS JOURNAL, 41, 1051 (1919).

divided metallic precipitate, extremely reactive with respect to water and air. From the reaction ratio they proposed the formula $NaZn_4$. Mathewson[5] obtained only the compound $NaZn_{12}$ by the method of thermal analysis. In the present paper the precipitate formed as mentioned above is analyzed and shown to have the composition $NaZn_4$. The results of a study of the reactions between this compound and oxygen, air and water are also presented.

Preparation of the Sodium Zinc Compound.—The apparatus used for the reaction of sodium upon zinc cyanide is shown in Fig. 1. Anhydrous ammonia gas, obtained from a small supply tank of liquid ammonia, to which pieces of sodium had been added, entered the reaction tube, R, through a tube, I, and condensed under a pressure of 10 cm. of mercury as shown by the gage P. Cooling was provided by a bath of liquid ammonia in the Dewar flask D, through which a current of air was bubbled to secure a still lower temperature. After 100 cc. of ammonia had condensed, about 0.5 g. of sodium, freshly cut under petroleum ether, immediately transferred to a weighing bottle filled with dry nitrogen and weighed, was added through the side tube O. Then the calculated amount of Kahlbaum's zinc cyanide was added slowly. Reaction occurred very rapidly and a dense black precipitate quickly settled out. That a gaseous product insoluble in water was not formed was shown in several cases by closing the clamp, G, and opening the clamp, H, for the duration of the reaction.

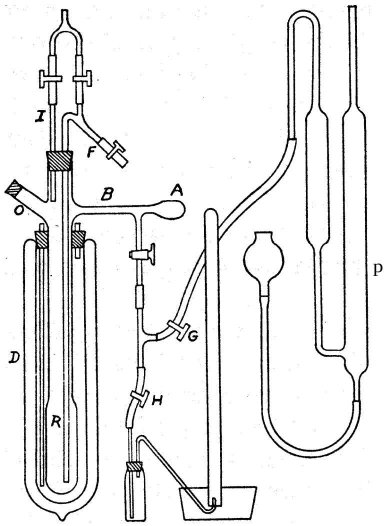

Fig. 1.—Apparatus used for the preparation of $NaZn_4$.

When the reaction was completed, the clear solution was removed and the precipitate washed as follows. With a small pressure on the system, a clamp on tube F was opened and the liquid above the precipitate forced out through tube F. By careful manipulation 90% or more of the liquid could be drawn off without loss of the solid. Fresh ammonia was now condensed and the process repeated. In this way the precipitate was washed seven or eight times. The last trace of ammonia in the reaction tube was allowed to evaporate against a slight pressure.

The product of the reaction was left in the form of a black powdered material. Samples for analysis were obtained by tipping the reaction tube until a suitable quantity had entered the collection tube A. The collection tube was then sealed off at B, evacuated to about 0.01 mm. of mercury and weighed. The sample was then dissolved in 6 *N* hydrochloric acid, using a technique similar to that described by Franklin.[6] The solution was analyzed for zinc and ammonia.

Composition of the Sodium–Zinc Compound.—An aliquot part of the acid solution was analyzed for zinc by precipitating and weighing as $ZnNH_4PO_4$. Another portion was analyzed for ammonia by distillation, after the addition of concentrated sodium

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[5] Mathewson, *Z. anorg.* Chem., 48, 196 (1906).

[6] Franklin, J. Phys. Chem., 15, 509 (1911).

hydroxide and collection of the distillate in 0.1 N HCl. No more than a trace of ammonia was found in any sample. The results of the zinc analyses are given in Table I.

TABLE I

COMPOSITION OF THE SODIUM–ZINC COMPOUND

Calculated for $NaZn_4$: Zn = 91.9%

No.	Sample, g.	$ZnNH_4PO_4$, g.	Zinc, g.	Zinc, %
30	0.2074	0.5155	0.1889	91.1
31	.1295	.3243	.1188	91.8
32a	.0778	.1960	.0718	92.3
32b	.0851	.2144	.0786	92.3
32c	.1479	.3700	.1356	91.7
20	.1058	.2636	.0966	91.3
23	.1046	.2635	.0965	92.3

The first three samples were prepared solely for the zinc analysis, the others were first treated in various ways. All samples, except 32, were prepared by adding zinc cyanide to a sodium solution in the ratio of 1 $Zn(CN)_2$ to 2.25 Na. This ratio, first determined by Kraus and Kurtz,[3j] was checked and found to be correct. In preparing Sample 32 the addition of zinc cyanide was stopped while the solution was still blue, so that a slight excess of sodium was present.

The results establish the formula $NaZn_4$ for the sodium zinc compound. The equation for the reaction is

$$4\ Zn(CN)_2 + 9\ Na = NaZn_4 + 8\ NaCN$$

A slight excess of sodium does not affect the composition of the precipitate. An excess of zinc cyanide, however, does change its composition. Thus by having a 20% excess of zinc cyanide present, the product analyzed once 98.1% of zinc and again, 99.3% of zinc.

Oxidation of the Sodium–Zinc Compound.—Kraus and Kurtz[3j] reported that this compound was very active toward air and water. Attempts were made to establish quantitatively the reactions taking place between $NaZn_4$ and dry oxygen, dry air, moist oxygen and moist air.

In most of the experiments the $NaZn_4$ was first prepared in a small reaction tube, the top of which was sealed before the final evaporation of the ammonia. The side arm of the reaction tube was then sealed to another tube which we shall call the oxidizing system. This system was also joined through stopcocks and glass tubing with an evacuating pump, a closed mercury gage and a buret. The top of the buret was also connected with a source of dry oxygen or air and the bottom was joined by rubber tubing to a leveling pear containing mercury. After the entire system had been evacuated to approximately 0.01 mm. of mercury, a measured volume of gas was allowed to enter from the buret. The process of the oxidation was followed by the decrease in pressure as shown on the mercury gage. The entire system was later calibrated so that the volume of gas in the system corresponding to any gage reading could be calculated. By subtracting the amount of gas in the system from the total amount let in, the volume used up at any stage of the reaction could be obtained. In a few cases the sample was weighed before and after oxidation, to get the weight of oxygen involved.

The oxidation reaction is divided into two distinct stages. At first oxygen is taken up rapidly, with considerable evolution of heat, but no noticeable change in the appearance of the sodium zinc takes place. This primary oxidation is followed by a secondary reaction which proceeds at a very slow rate for a long period of time, accompanied by a change in the color of the substance from black through gray to white.

Dry air acts in the same way as dry oxygen. Moist air or moist oxygen accelerates the oxidation so much that the two stages are not apparent. A higher temperature also speeds up the secondary reaction. The data for these statements are given in Table II.

TABLE II

OXIDATION OF $NaZn_4$ BY DRY OXYGEN AT ROOM TEMPERATURE FOR ONE-HALF HOUR

No.	$NaZn_4$, g.	Oxygen, cc., (S. T. P.)	Oxygen, g.	Oxygen, mg atoms	$NaZn_4$, mill. moles	Ratio, mg atoms of O to mill. moles of $NaZn_4$
3	0.4452	10.60	0.0152	0.950	1.565	0.61
5	.6460	12.76	.0182	1.138	2.270	.50
6	.3506	7.02	.0100	0.625	1.232	.51
7	.4101	8.37	.0120	.750	1.441	.52
8	.6084	10.66	.0152	.950	2.138	.45
10	.4701	14.12	.0202	1.263	1.652	.76
12	.4155	9.72	.0139	0.869	1.460	.59
Dry Air at Room Temperature						
30	0.1244	...	0.0031	0.194	0.437	.45
31	.1295	...	.0036	.225	.455	.49
Dry Oxygen at Room Temperature for 4 Weeks						
7	0.4101	12.18	0.0174	1.088	1.441	0.76
8	.6084	18.38	.0263	1.644	2.138	.77
Dry Oxygen at 150–200° for 25 Hours						
5	0.6460	93.95	0.1342	0.839	2.270	3.70
Moist Oxygen at Room Temperature						
4	0.4418	21.51	0.0307	1.919	1.553	1.2
14	.1185	7.13	.0102	0.638	0.417	1.5
Moist Air at Room Temperature						
16	0.5274	...	0.0912	5.700	1.854	3.1

The most remarkable feature of the oxidation experiments is that the $NaZn_4$ rapidly takes up enough oxygen to form sodium monoxide. Then apparently the zinc is slowly oxidized. With moisture both the sodium and part of the zinc react rapidly with oxygen, the heat liberated increasing the speed of the reaction. Tests for peroxides were made on several samples, oxidized in different ways, without obtaining any evidence of their formation. That the amount of oxygen taken up by the sample varied considerably was' due to variation in conditions. For instance, if the oxygen were let in rapidly, considerably more heat was developed and more oxygen absorbed in a given time than when the gas was let in slowly. A further study and standardization of the conditions of oxidation are necessary for more definite conclusions.

The Action of Water and Dilute Acid upon $NaZn_4$.—The reaction between $NaZn_4$ and water, and also dilute acid, was investigated by allowing a small amount of water, or acid, to enter the evacuated collection tube containing a known weight of sample. The hydrogen liberated by the reaction was removed by means of a Toepler pump and analyzed by explosion with air. With water the reaction, even at first, was a slow one, continuing with decreasing rate for some time. Thus during the first week approximately 20 cc. of hydrogen per gram of sample was liberated each day. At the end of a month about 1 cc. of hydrogen per day was formed. With dilute acid the reaction was over in a short time. The total amount of hydrogen liberated is given in Table III.

TABLE III

HYDROGEN LIBERATED BY THE REACTION DURING A PERIOD OF TWO MONTHS

	With water		With 6 *N* HCl	
Expt. no.	18	19	32a	32b
$NaZn_4$, g.	1.1316	1.9280	0.0778	0.1479
Hydrogen, cc. (S. T. P.)	189.0	334.6	27.4	53.1
Hydrogen, g.	0.0170	0.0301	0.0025	0.0048
Equiv. H_2 per mole $NaZn_4$	4.2	4.4	9.0	9.1

The reaction of the sodium in $NaZn_4$ upon water and of the sodium hydroxide formed in this way upon zinc would account for less than half of the hydrogen obtained. Evidently the zinc reacted directly with water to furnish this extra hydrogen.

The hydrogen liberated when the sample was treated with acid is equivalent to the total sodium and zinc present. This result may be taken as additional evidence of the composition of the compound.

Summary

The product formed when zinc cyanide is added to a solution of sodium in liquid ammonia has been shown by analysis to have the composition $NaZn_4$. This compound reacts with oxygen or air in two stages, the speed of the secondary reaction being increased by the presence of moisture or by heating. Reaction of the compound with dilute acid liberates nine equivalents of hydrogen per mole of $NaZn_4$; with water, approximately 4.5 equivalents of hydrogen are liberated in two months.

CINCINNATI, OHIO

[Contribution from the Chemical Laboratory of Stanford University]

A STOPCOCK IN WHICH CONTAMINATION BY GREASE IS PREVENTED AND ITS APPLICATION TO A PROBLEM IN GAS TECHNIQUE

By Herman C. Ramsperger[1]

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Vapors from stopcock grease are always more or less objectionable in high vacuum work, but greased stopcocks have frequently been tolerated when gases under moderate pressure were to be transferred through such a system in roughly controlled amounts. The objection to stopcock grease is more serious when organic vapors are to be handled, for in many cases these vapors are taken up in appreciable amounts by the stopcock grease. This is the case in a problem in reaction velocity which the author wished to undertake, and the apparatus here described was successfully used in that work.

The principle is illustrated by Fig. 1A.

This stopcock is of the hollow plug type. The ground portion is about 4-cm. long. A small groove is ground on the outside of the plug, completely encircling it at about two-thirds of the way down the ground portion as shown at a. Two vertical grooves are etched on the inside of the bore of the stopcock from the top of the ground portion down sufficiently far to reach the circular groove when the plug is in place. They are shown in the cross-sectional diagram, Fig. 1B, at b. They are about 1 mm. wide and probably about 0.1-mm. deep. They are produced by etching with concentrated hydrofluoric acid for about twenty minutes.

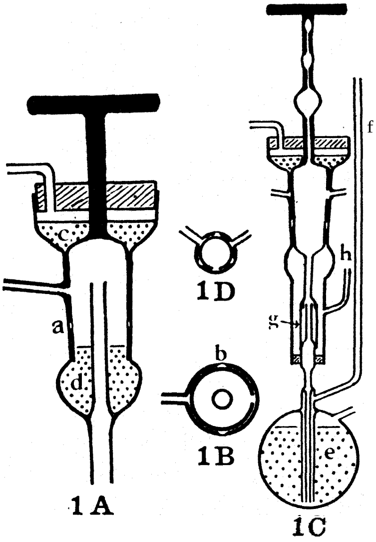

Fig. 1.

The stopcock is assembled as follows. A very small amount of stopcock grease is applied to the lowest edge of the ground portion of the bore and the plug inserted with the hole of the plug in line with the side opening on the bore. If now the system is evacuated, mercury from above the plug at c will flow down the two vertical grooves and into the circular groove. Gas flowing through the stopcock cannot come in contact with the stopcock grease on the lower ground portion, for it is protected between the ground surfaces by the ring of mercury, and from the inside by the mercury at d. To close the stopcock the plug is turned through 180° as shown in Figure 1B. In this process a very small droplet of mercury falls through the hole as the hole passes one of the grooves. It is apparent that the stopcock will not allow gas to pass if the pressure on either side of the stopcock is a few cm. less than the external pressure forcing the mercury into the grooves.

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[1] National Research Fellow in Chemistry.

The success of such a stopcock depends on the fact that surface tension prevents the mercury from going beyond the edges of the grooves, which it will not do if the surfaces are sufficiently close fitting. If, however, they fit very tightly, the stopcock cannot be turned. The purpose of the grease in the lower portion is to give a slight separation so that the stopcock may be turned easily. It was found that from 40 to 50 cm. difference in pressure was the upper limit for which the mercury would not leak through and the stopcock could yet be turned. It was, therefore, necessary to control the external pressure by placing a rubber stopper over the top of the stopcock, thereby making it possible to control the pressure on the mercury at c. The hole in the stopper through which the handle of the plug passes is greased and remains airtight.

It was convenient in the study of the thermal decomposition of the gas methyl isopropyl di-imide to be able to introduce a measured amount of gas from a supply bulb into the reaction cell, and to measure the pressure in the cell immediately and at intervals during the reaction. In another research it was necessary to introduce into the reaction cell a definite pressure of azomethane gas mixed with varying amounts of some inert gas, and then to follow the decomposition of the azomethane by pressure measurements. If this were attempted using ordinary greased stopcocks the partial pressure of azomethane would change during handling of the gases, due to absorption by the grease.

An application of the above described stopcock was devised for these experiments. It is illustrated in Figs. 1C and 1D.

The body of the stopcock is made as in Fig. 1A except that there are two side tubes and three vertical grooves as indicated in Fig. 1D. When this stopcock is in the closed position (Fig. 1D) it may be used as a McLeod gage, mercury being forced up from the bulb, e. Accuracy over a wide range of pressures is secured by placing bulbs of varying size in the handle of the stopcock. The gage is calibrated by determining the volumes to fixed points on the capillaries between the bulbs, and to a fixed point in the tube below the hollow plug. The one used in the experiments referred to has a total volume of 15.2 cc. and can measure pressures from 0.06 to 30 mm. with an accuracy varying between 0.2 and 2%. The tube, f, leads to a high vacuum. This tube is larger than the capillaries in the handle, so that with the gage evacuated the mercury in the tube, f, rises to a higher level than in the capillary. When the mercury is at one of the fixed points on the capillaries the mercury levels on the tube, f, are taken as the positions of zero pressure.

To allow the stopcock to turn and yet keep the mercury bulb, e, stationary, a rubber tubing connection is made at g. The space surrounding it is evacuated through the tube, h. When the mercury has once been run up through this rubber connection and has filled the rubber tube and the inner glass tube, no gas in the gage comes in contact with rubber tubing.

In using the device for the azomethane research, azomethane was introduced through the left tube. The flow could be controlled readily, since the gas could be made to pass between the ground surfaces to reach the hole. The stopcock was closed and the pressure measured. Azomethane was pumped out of the left tube and an inert gas under pressure was then similarly admitted. The total pressure was then determined. The gases were thoroughly mixed by the compression and expansion during the pressure measurement. The mixed gases were admitted to the reaction cell, which was attached close to the right-side tube. The stopcock was then closed and the pressure read at liberty. At any predetermined time the stopcock was opened for a few seconds and another pressure measurement made. The rate of this reaction could thus be followed, since an increase in pressure at constant volume occurs in the reaction.

It is evident that at no time after the gases were once admitted to the gage did they come in contact with grease. The device is very compact when one considers the number of operations to be performed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE THERMAL DECOMPOSITION OF METHYL ISOPROPYL DI-IMIDE: A HOMOGENEOUS UNIMOLECULAR REACTION. THE THERMAL DECOMPOSITION OF HYDRAZOIC ACID AND METHYL AZIDE

BY HERMAN C. RAMSPERGER[1]

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It is important that present theories of unimolecular reaction velocity should be thoroughly tested with a wide variety of reactions. All homogeneous unimolecular gas reactions so far discovered involve rather large molecules. Their reaction rate is too fast to be accounted for without ascribing to some of them as large a number of internal degrees of freedom as can be justified, while others require but few degrees of freedom. The decomposition of nitrogen pentoxide cannot at present be accounted for in this way, but the low-pressure data may still be questionable.

The author had previously found that the two azo compounds, azomethane[2] and azo-isopropane[3] decompose in a homogeneous unimolecular manner. A new azo compound, methyl *iso*propyl di-imide was recently prepared[4] by the author to provide an additional test of unimolecular reaction rate theories. Its decomposition will be shown to be first order at high pressures. However, the rate constant becomes lower at low pressures, as was also the case with azomethane.[5]

A unimolecular reaction involving a smaller molecule with a more limited number of degrees of freedom would provide another valuable test of reaction rate theories. For this reason the decomposition of hydrazoic acid and methyl azide was studied.

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[1] National Research Fellow in Chemistry.

[2] Ramsperger, THIS JOURNAL, **49, 912 (1927).**

[3] Ramsperger, *ibid.,* **50, 714 (1928).**

[4] Ramsperger, *ibid.,* **51, 918 (1929).**

[5] Ramsperger, *ibid.,* **49, 1495 (1927).**

The Thermal Decomposition of Methyl Isopropyl Di-imide

Methyl *iso*propyl di-imide was prepared as described in a previous publication.[4] The thermal decomposition was carried out at pressures ranging from 5.8 $\times 10^{-3}$ cm. to **13.12** cm. and at temperatures ranging from 250 to 332°.

Nature of the Reaction Products.—A rough analysis of the products of decomposition in Expt. 34 (Table I) was made. The final pressure in this experiment (and all other experiments with this sample) was **2.18** times the initial pressure at constant volume. We may write equations for the likely reactions analogous to those of the other two azo compounds previously studied. The main reaction products in these cases were nitrogen and a hydrocarbon as shown, for example, in the equation $CH_3N{=\!=}NCH_3 = N_2 + C_2H_6$. In this new mixed azo compound, however, an analogous reaction may yield either a single hydrocarbon or a mixture of hydrocarbons according to whether the two radicals combine at the instant of disruption of the molecule or the separate radicals combine at random later.

The former case gives only butane and nitrogen. In the latter case we may expect combinations between two methyl radicals, between two isopropyl radicals and between methyl and isopropyl radicals. The equations for the two mechanisms are then as follows

$$CH_3N{=\!=}NC_3H_7 = N_2 + C_4H_{10} \qquad \text{(a)}$$

$$CH_3N{=\!=}NC_3H_7 = N_2 + xC_2H_6 + yC_4H_{10} + zC_6H_{14} \qquad \text{(b)}$$

Since the final pressure is greater than twice the initial pressure as would be required by both of these equations, there is a side reaction, as was also the case with the other azo compounds. Analogous side reactions are

$$2CH_3N{=\!=}NC_3H_7 = 2N_2 + C_2H_4 + 2C_3H_8 \qquad \text{(c)}$$

$$CH_3N{=\!=}NC_3H_7 = N_2 + CH_4 + C_3H_6 \qquad \text{(d)}$$

The gas to be analyzed was collected in a 250-cc. flask which had a manometer attached and had a tube sealed to the bottom. Liquid air, carbon dioxide snow and freezing mixtures were placed around this tube. After surrounding the tube with a constant temperature bath, the manometer pressures were read repeatedly until no further change was noted. This usually required only ten or fifteen minutes but a much longer time was usually taken to be sure of a constant reading. . The initial pressure of the gas was 10.98 cm. At −78°, 17.6% of the gas was condensed by means of ether–carbon dioxide mixture. Most of this condensed out between —20 and —50". Liquid air condensed **43.4%.** The vapor pressures of all of the possible reaction products are known at least approximately. Hexane is the only hydrocarbon that should condense out at temperatures above —78". Methane and nitrogen are the only gases that should remain uncondensed with liquid air. Since Reaction b is the only one producing hexane, the main reaction is to be represented by Equation b. If the side reaction c is to account for the final pressure, then 54.1% of the gas should be condensable with liquid air, while if Reaction d occurs only 45.9% of the gas should condense. Since the experimental result is even slightly lower than the latter value, it seems that Reaction d is the probable side reaction. An analysis made by the freezing out of vapors is not expected to be very accurate, but if a choice is to be made among these four reactions, the differences in the pressures expected are sufficiently great for this method to give the correct result. The 17.6% condensed at −78° is somewhat higher than one might expect. Collisions between the larger isopropyl radicals will occur more often than collisions between methyl radicals. If the diameter of an isopropyl radical be taken as 2.5 times that of a methyl radical and all combinations of the radicals are taken to be equally probable, then kinetic theory equations for the number of collisions[6] show that 37.1% of the mixed gases should be hexane and 14% of all of the gas should be condensable. It seems likely that the difference between the latter value and 17.6% may be due to butane and propylene dissolving in the condensed hexane, especially since the partial pressure of the butane is about two-thirds of its saturation pressure for this temperature.

Preparation and Purification.—Methyl isopropyl di-imide was prepared and purified in the manner described in a previous paper by the author.[4] Two different samples were used in this research. Experiments 1 to 30 (Table I) were made with the first sample and Expts. 31 to 47 were made with the second sample. An examination of the rate constants shows that the second sample gave the same rate constants as the first sample. However, the final pressures were about 2.12 times the initial pressure for Sample 1, and 2.18 times the initial pressure for Sample 2. The rate constants were calculated on the basis of the final pressures obtained. It is likely that the first sample contained a small amount of impurity, probably a hydrocarbon of similar boiling point.

Reaction Rate Measurements.—The same pyrex reaction cell, surrounded by mercury vapor boiling under a constant pressure, that was used with the previously studied azo compounds was used here. In addition, a similar apparatus made entirely of quartz was used in Expts. 1, 2, 31, 32 and 33. Experiments at pressures above 3 cm. were made exactly as with azomethane.[2] Experiments at low pressures were made with a combination of stopcock and McLeod gage described in the preceding article.[7] The first reading could be made within several seconds after the McLeod gage was open to the cell, and in only a few of the most rapid experiments was a correction necessary for the decomposition before this reading was made. The McLeod gage was kept closed between readings, and opened for only five to ten seconds before each pressure reading was made. The calculation of the partial pressure of the methyl *iso*propyl di-imide in the reaction cell was somewhat simpler than was the case with the apparatus used in the previous researches.

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[6] Tolman, "Statistical Mechanics," The Chemical Catalog Co., New York, 1927, p. 71.

[7] Ramsperger, This Journal, 51, 2132 (1929).

Let P be the pressure read on the McLeod gage and *AP* the pressure increase during the preceding time interval. Let V_1 and T_1 be the volume and temperature of the McLeod gage and V_2 and T_2 the volume and temperature of the reaction cell. Then P', the total pressure in the reaction cell just before the reading, is given by $P' = P + \Delta P V_1 T_2/V_2 T_1$. Now the increase in pressure from the previous reading at time t' to the reading at time t divided by ***1.18*** (or ***1.12*** for the first sample) gives the reduction in pressure of the methyl isopropyl di-imide in the cell. If P'_{At} represents the partial pressure of methyl isopropyl di-imide before the reading at t' and $P_{At'}$ represents its partial pressure at the end of the previous reading, we have

$$P'_{At} = P_{At'} - (P_{t'} - P'_t)/1.18 \quad \text{and} \quad P_{At} = P'_{At}\, P_t/P'_t$$

The rate constant is then given by

$$K = \log_{10} \frac{P_{At'}}{P'_{At}} \times \frac{2.303}{t - t'}$$

where t and t' are given in seconds.

Experimental Results.—A summary of all of the experiments is given in Table I.

TABLE I

SUMMARY OF ALL EXPERIMENTS

Expt.	Temp., °C.	Init. press., cm.	Av. $K \times 10^3$	Expt.	Temp., °C.	Init. press., cm.	Av. $K \times 10^3$
37	250.0	4.53	0.0409	47	300.0	0.709	1.69
36	259.1	6.54	.088	1	300.0	0.444	1.33
24	260.0	0.690	.0544	2	300.0	0.0378	0.97
22	260.0	0.142	.050	18	300.0	0.0058	.445
35	270.0	9.32	.220	32	310.0	4.04	3.94
38	270.0	3.24	.210	43	310.0	0.604	3.22
39	270.0	0.673	.171	30	310.0	.195	2.47
40	270.0	.637	.157	4	310.0	.0938	1.98
9	270.0	.128	.117	5	310.0	.0215	1.39
10	270.0	.0583	.107				
41	270.0	.0430	.106	45	322.0	.690	6.90
25	270.0	.0123	.077	8	322.0	.390	5.54
				6	322.0	.124	4.56
34	285.0	13.12	.714	15	322.0	.091	5.01
31	285.0	3.29	.686	7	322.0	.040	3.84
33	285.0	2.53	.600	46	322.0	.0233	3.50
42	285.0	0.781	.533	16	322.0	.0133	3.25
29	285.0	.194	.379				
28	285.0	.152	.426	19	332.0	.134	9.80
12	285.0	.136	.346	20	332.0	.0175	5.53
13	285.0	.0606	.325	21	332.0	.0080	4.20
26	285.0	.0168	.297				

The complete data of two typical experiments are given in Table II.

Discussion

Experiments 28, 29 and **30** were made with sufficient pyrex tubing in the cell to increase the surface five-fold. Since the rates fall in line with

TABLE II

COMPLETE DATA OF TWO EXPERIMENTS

Expt. 39. $V_1T_2/V_2T_1 = (15.2 \times 543)/(210 \times 298) = 0.130$

t, min.	P, cm.	P′	P'_A	P_A	$K \times 10^3$
0	0.673	0.673	0.673	0.673	...
11	.743	.752	.606	.599	0.163
21	.809	.817	.536	.531	.185
32	.863	.870	.479	.475	.160
50	950	.961	.392	.388	.178
75	1.043	1.055	.299	.296	.174
120	1.162	1.177	.182	.180	.180
159	1.221	1 228	.124	.123	.159

Expt. 46. $V_1T_2/V_2T_1 = 15.2 \times 595/210 \times 298 = 0.142$
Decomposition in filling cell = 0.0004 cm.

t, min.	P, cm.	P′	P'_A	P_A	$K \times 10^3$
0	0.02378	0.02378	0.0229	0.0229	..
1.33	.02968	.03052	.0172	.0168	3.58
2.75	,03401	.03463	.0126	.0124	3.38
4.25	,03779	.03833	.0087	.0086	3.94
6	.04028	.04064	.0062	.0062	3.12
45	.04599	.04680	.0007	.0007	..

the experiments made with the empty cell and with those made in the quartz cell, the reaction is homogeneous and not influenced by the walls.

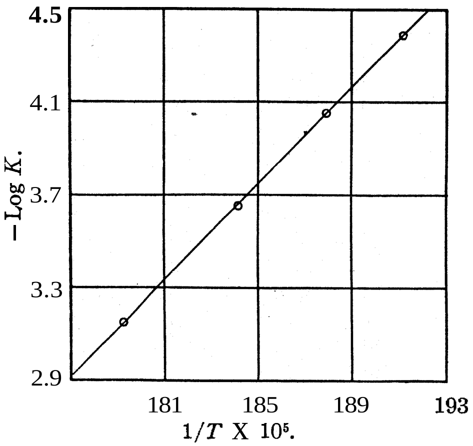

Fig. 1.

It is apparent that within experimental error and reproducibility the decomposition is first order in any given experiment. It is also apparent that the rate constant varies with the initial pressure, being lower for lower initial pressures. It does, however, approach a constant value at the higher pressures and lower temperatures as, for example, at 270 and 285°. Experiments were made at 250, 259.1, 270 and 285" at sufficiently high pressures to approach the value which would be obtained for very high pressures. The log of the rate constants for these experiments is plotted against $1/T$ in Pig. 1. These points should fall on a straight line according to the Arrhenius equation for the temperature coefficient of reaction velocity, namely, $d \ln K/d(1/T) = Q/R$. The line drawn through the points in Pig. 1 is a straight line. Q is found to be 47,480 cal. per mole. The equation for the rate constant is $2.72 \times 10^{15} \times e^{-47480/RT}$. However, the asymptotic values of the rate constants have not quite been reached at the highest pressures studied. We may take roughly $2.80 \times 10^{15} \times e^{-47480/RT}$ as the best value of the rate constant for very high pressures.

This reaction is evidently very similar to that of azomethane, which was shown to be first order at high pressures and to fall off in rate at lower pressures. With methyl isopropyl di-imide the high pressure rate is maintained to somewhat lower pressures than with azomethane. The more complex azo-isopropane showed no dropping in rate at the lowest pressures studied. A collision theory of activation developed by Rice and the author[8] (Theory II) was shown to be in agreement with the experimental data on azomethane.[9] Kassel[10] has also developed a theory (Theory III) which is very similar to Theory II of Rice and the author. Another theory (Theory I) of Rice and the author, which is an extension of the theory of Hinshelwood and Lindemann[11] to low pressures, does not fit the azomethane data. It has also been shown by Kassel[10] and by Rice and the author that several reactions studied by Hinshelwood and his co-workers cannot be accounted for as well on Theory I as on Theory II or III. More recently Rice[12] and Kassel[13] have given quantum treatments based on Theories II and III. The quantum treatments are more difficult to apply and for large molecules are not sufficiently different from the earlier classical theories for experimental data of the usual accuracy to decide between them. There is also no appreciable difference between Theories II and III for a molecule having a large number of degrees of freedom involved in the reaction, as is the case with the azo compounds. I will therefore use Theory II to interpret the decomposition of methyl isopropyl di-imide.

Equation 19 of reference 8 (*cf.* p. 1624) has been integrated graphically, using a value of 33 for n, and values of 543, 573 and 603 for T, corresponding to 270, 300 and 330°. E is 46,900 cal. per mole (from Equation 20 of reference 8). Log K/K_∞ is then calculated for a series of values of β_2/p. The experimental data are plotted as in Fig. 2. The theoretical curves are then found to fit the data if the molecular diameter be taken as 6×10^{-8} cm. The upper theoretical curve is for 270°, the middle curve for 300° and the lower curve for 330°. Most of the experimental points from 270 to 332° fall within the region bounded by the theoretical curves. It may also be observed that low temperature points fall above high temperature points. The small differences between the theoretical curve and experimental points should be ascribed to experimental errors of the indi-

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[8] Rice and Ramsperger, THIS JOURNAL, 49, 1617 (1927).

[9] Rice and Ramsperger, *ibid.*, 50, 617 (1928).

[10] Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

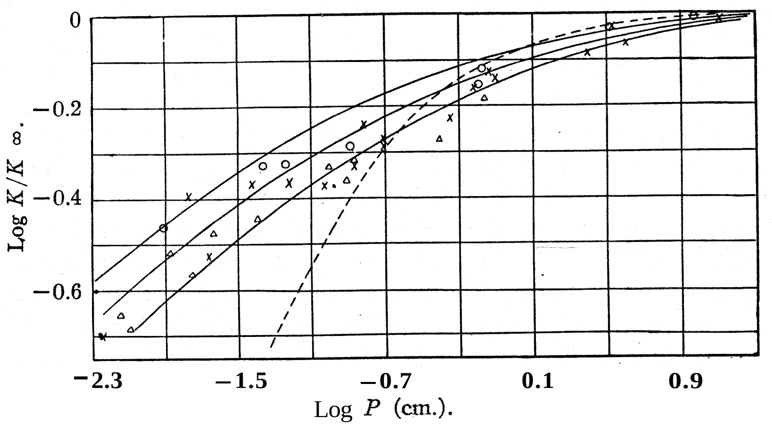
[11] Hinshelwood, *Proc. Roy Soc. London*, **113A**, 230 (1928).

[12] Rice, *Proc. Nat. Acad. Sci.*, **14**, 114 (1928).

[13] Kassel, *J. Phys. Chem.*, **32**, 1065 (1928).

vidual points and to a small possible error in K_∞ as calculated from Equation 1. The agreement is therefore as good as the experimental accuracy would justify.

The author would like to call attention to the significance of this agreement. If, for example, Theory I be applied with the same value for n and for the molecular diameter as used for Theory II, the dotted curve of Fig. 2 is obtained. This curve has the wrong shape and so cannot be made to fit all of the experimental points by changing either the diameter or the number of degrees of freedom. The curves for Theory II have now been shown to fit the low pressure data for the two azo compounds, azomethane and methyl *iso*propyl di-imide. They have also been shown to fit the data for diethyl ether and dimethyl ether.[9] The only other reaction that has been carried to low enough pressures to test theories of reaction velocity is the decomposition of nitrogen pentoxide. Here, however, the data of the various investigators do not agree among themselves, and Loomis and Smith[14] have recently shown that the methods used in these experiments produce very large errors due to absorption and occlusion. Very recently it has been reported that the rate constant of this reaction falls off even at several mm. pressure,[15] so conclusions regarding this reaction must be withheld until the low pressure data are confirmed. It is also significant that all of the various theoretical treatments that are based on the assumption that reaction occurs whenever a definite amount of energy becomes localized in one or at most several degrees of freedom, give the correct shape of curve. Normal molecular diameters are used



○, Experiments at 270"; ×, experiments at 285–310°; A, experiments at 322 and 332°.

Fig. 2.

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[14] Loomis and Smith, This Journal, 50, 1864 (1928).

[15] Rice, Urey and Washburn, *ibid.*, 50, 2402 (1928).

and the number of degrees of freedom required is not greater than is allowable in applying these theoretical treatments.

If, however, reliable data on the decomposition of nitrogen pentoxide do not agree with these theories, we may expect to find other unimolecular reactions, especially of inorganic molecules, which will disagree. It is possible that the assumptions made in the derivation of the theories regarding energy transfer both between molecules at collision and between internal degrees of freedom are approximately obeyed in the organic molecules and not in the others.

Data on the three azo compounds studied by the author are collected in Table III. P(cm.) is the pressure range studied, T the temperature range, A and Q are the quantities in the expression for the rate constant at high pressures, $K_\infty = Ae^{-Q/RT}$ and n is the number of degrees of freedom required by Theory II.

TABLE III

COLLECTED DATA FOR THREE AZO COMPOUNDS

Compound	P, cm.	T, °C.	A	Q, cal.	n
$C_2H_6N_2$	0.0259 to 70.79	278 to 327	1.07×10^{16}	51,200	25
$C_4H_{10}N_2$	0.0058 to 13.12	250 to 332	2.80×10^{15}	47,480	33
$C_6H_{14}N_2$	0.025 to 4.60	250 to 290	5.6×10^{13}	40,900	>40

The heat of activation of the new compound is intermediate between that for dimethyl di-imide and di-isopropyl di-imide. If now the decomposition of these azo compounds occurs by the breaking of a single bond, then we may expect the heat of activation of methyl isopropyl di-imide to be very nearly that of di-*iso*propyl di-imide, namely, 40,900 cal. per mole, for the reaction will occur at the weaker isopropyl bond and the interchange of methyl for *iso*propyl should not greatly alter the binding energy of the *iso*propyl bond. If, however, the reaction occurs by the simultaneous rupture of both bonds, then we may expect an intermediate heat of activation, and this is the experimental result. From the fact that the main reaction gives a mixture of hydrocarbons, we conclude that the two radicals are not combined at the instant of reaction but are separately dislodged and combine at random later.

The Thermal Decomposition of Hydrazoic Acid

Anhydrous hydrazoic acid vapor was found to decompose at 290° with measurable velocity. A white solid, probably ammonium azide, was formed and a gas, probably nitrogen, which was not condensable in liquid air was also produced. Only a small increase in pressure accompanied the reaction, so that the rate was followed by determining the percentage of gas not frozen out by liquid air. Three experiments, all at 290° and about 4-cm. pressure, showed that 9 to 11% of the hydrazoic acid was decomposed in twenty-five minutes, When pyrex tubing was placed in the reaction cell in sufficient amount to increase the surface to four times the original surface, three similar experiments showed that 12% was decomposed in eight minutes, 22% in twenty-five minutes and 31% in thirty-four minutes. While no great accuracy can be claimed for these experiments, they show conclusively that the reaction is catalyzed by the walls of the vessel. Since the reaction is not homogeneous it cannot be used to test gas phase reaction theories and so the reaction was not studied further.

The Thermal Decomposition of Methyl Azide

Methyl azide (CH_3N_3) was prepared from sodium azide and methyl sulfate. Five experiments were carried out at 245°. The complete decomposition gave a final pressure of 1.55 times the initial pressure. No analysis of the products of reaction was made but a white solid formed similar to that from hydrazoic acid. The reaction may very likely be the following, $2CH_3N_3 = C_2H_4 + 2HN_3$. The reaction rate so measured by the pressure increase was not influenced by increasing the wall surface and is therefore homogeneous. The reaction rate was first order during a given experiment but the rate constant became much lower at low pressures. A summary of the five experiments is given in Table IV.

TABLE IV

SUMMARY OF EXPERIMENTS

Expt.	5	4	1	3	2
Init. press., cm.	5.75	4.06	3.37	0.226	0.0484
Av. $K \times 10^3$	1.98	1.64	1.50	0.52	0.31

The reaction is somewhat uncertain because of the fact that it may be followed by the decomposition of hydrazoic acid, and the formation of the white solid would lead to inaccuracies at higher pressures. It seems likely, however, that this is really another homogeneous unimolecular reaction the rate of which falls off at low pressures.

The author wishes to take this opportunity to express an appreciation of the interest and encouragement Professor Gilbert N. Lewis has generously given throughout the author's researches on azo compounds made at the University of California and elsewhere.

Summary

The thermal decomposition of methyl *iso*propyl di-imide was studied over a temperature range of 250 to 332° and a pressure range of 0.0058 to 13.12 cm. The reaction has been found to be homogeneous and first order at high pressures, but the rate constant falls off at pressures below several cm. The high-pressure rate constant is given by the expression $K_\infty = 2.80 \times 10^{15} \times e^{-47480/RT}$. Theory II of Rice and the author has been found to fit the data if the molecule be assumed to have 33 degrees of freedom. The significance of this agreement is discussed. All unimolecu-

lar reactions (with the possible exception of nitrogen pentoxide) agree with theories based on the assumption that reaction occurs whenever a definite amount of energy becomes localized in one or, at most, several degrees of freedom.

The thermal decomposition of hydrazoic acid was found to be catalyzed by the pyrex walls of the reaction vessel.

The thermal decomposition of methyl azide was found to be homogeneous and first order during a given experiment but the rate constant becomes lower at lower initial pressures.

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[Contribution from the Chemistry Laboratory of the University of Michigan]

SOME THIOPHENE ANALOGS OF DI-, TRI- AND TETRAPHENYLMETHANE COMPOUNDS[1]

By Wesley Minnis

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In the course of an attempt to extend the results of a previous investigation[2] of free radicals containing the thiophene ring, studies were made of various analogs of di-, tri- and tetraphenylmethane compounds in which one phenyl group was replaced by the thienyl group.

In general, methods of synthesis used in the benzene series were successfully applied. Usually the thiophene analogs were isolated with more difficulty, probably because of the greater reactivity of the thiophene nucleus, which tends toward the formation of by-products. After isolation, decomposition often occurred under conditions which do not similarly affect the phenyl compounds. For example, phenylthienyl ketone dichloride could not be distilled under reduced pressure without decomposition, whereas benzophenone dichloride is readily purified in such manner. The diphenylcarbinol halides have been made and are moderately stable, but attempts to prepare phenylthienylcarbinol halides resulted in deep-seated decomposition. The reduction of diphenylthienylcarbinol gave only a 50% yield of methane as contrasted with the practically quantitative yield of triphenylmethane from its carbinol. Diphenylthienylcarbinol halides were much less stable than the triphenylcarbinol halides, and the same was true of the corresponding free radicals.

The instability of the free radical, diphenylthienylmethyl, was reminiscent of the behavior of phenylthioxanthyl,[3] and it is tentatively suggested

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[1] This article is an abstract of Part II of the dissertation submitted to the faculty of the University of Michigan, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. 1922.

[2] Gomberg and Jickling, This Journal, 35, 446 (1913).

[3] Gomberg and Minnis, *ibid.*, 43, 1940 (1921).

that the presence of a bivalent-ring sulfur atom in its structure confers instability upon a free radical.

Of novel interest may be noted the preparation of a **di-triphenylmethyl-dithienyl** by a peculiar side reaction during a Grignard reaction; and of a-naphthylphenylthienylcarbinol, one of the few asymmetric **triarylcar**binols so far described.

Phenylthienyl Ketone **Dichloride,** $C_6H_5CCl_2C_4H_3S$.—Phenylthienyl ketone was prepared by the method described in the literature[4] but with higher yield than heretofore claimed, namely, 87%. A mixture of 19 g. of ketone and 22 g. (5% excess) of phosphorus pentachloride was heated at 60 to 80° for one hour. The phosphorus oxychloride formed in the reaction was distilled under reduced pressure and the partial vacuum maintained for one hour in order to remove excess pentachloride. The residual liquid could not be distilled under 20 mm. pressure without decomposition.

Anal. Calcd. for $C_{11}H_8Cl_2S$: Cl, 29.18. Found: Cl, 29.39.

Phenylthienylcarbinol, $C_6H_5CHOHC_4H_3S$.—The procedure of Montagne[6] for reducing a ketone to the corresponding carbinol by means of zinc dust and sodium alcoholate gave a product with sulfur content 3% under the theoretical. The method of Cohen[6] gave good results. To 5 g. of ketone dissolved in 40 cc. of alcohol and 10 cc. of concd. ammonium hydroxide solution was added 10 g. of aluminum amalgam and the mixture was refluxed for six hours. After cooling and filtration, the filtrate was poured into water, whereupon crystals separated after long standing. Recrystallized from ether, the crystals melted at 57 to 58°. Non-identity with the ketone was proved by a mixed melting point.

Anal. Calcd. for $C_{11}H_{10}OS$: C, 69.43; H, 5.30; S, 16.86. Found: C, 69.29; H, 5.23; S, 17.09. *Mol. wt.* Calcd.: 190. Found (cryoscopic in benzene): 195, 187.

Attempts to prepare the carbinol halides by passing dry hydrogen chloride or hydrogen bromide into solutions of the carbinol produced dark-colored oils which evolved gases while drying in a vacuum desiccator, leaving black lava-like solid residues.

Diphenylthienylcarbinol $(C_6H_5)_2C(OH)C_4H_3S$.—This has been described by Thomas? and Gomberg and Jickling[2] as prepared from benzophenone and the Grignard reagent from iodothiophene. A slightly higher yield was obtained by synthesis from phenylmagnesium bromide and phenylthienyl ketone, and the product melted at 131°, higher than either of the temperatures previously reported. Condensation of benzophenone dichloride with thiophene in carbon disulfide solution by means of aluminum chloride gave a much lower yield.

When boiled with formic acids the carbinol was reduced to the methane.9 About half of the carbinol, however, reacted to form a new compound, m. p. 174°, which gave analytical values corresponding to the methane but had a molecular weight of about double that of the methane.

Diphenylthienylcarbinol Bromide $(C_6H_5)_2CBrC_4H_3S$.—A solution of the carbinol in benzene or a suspension in low-boiling petroleum ether was saturated with dry hy-

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[4] Comey, *Ber.*, 17,790 (1884).

[5] Montagne, Rec. *trav.* chim., 25,402 (1906).

[6] Cohen, ibid., **38,** 86 (1919).

[7] Thomas, *Bull. soc.* chim., 5, 730 (1909); Thomas and Couderc, *ibid.*, 23, 326 (1918).

[8] Kauffmann and Pannwitz, Ber., 45,766 (1912).

[9] Levi, ibid., 19, 1623 (1886).

drogen bromide. A few lumps of calcium bromide were added to take up the water formed in the reaction. After filtration and evaporation under reduced pressure, crystals of melting point 110 to 111° were obtained. Originally only slightly colored, they quickly turned deep purple, even in a sealed tube in the dark.

Anal. Calcd. for $C_{17}H_{13}BrS$: Br, 24.31. Found: Br, 24.30, 24.09.

Diphenylthienylcarbinol Chloride.[2]—Best results were obtained by suspending the carbinol in petroleum ether with a few lumps of calcium chloride and slowly passing in dry hydrogen chloride to saturation. The solution was evaporated under reduced pressure and the crystals were washed with very small amounts of ice-cold petroleum ether and dried in a current of dry air at room temperature. They melted at 80 to 81° and the yield was 90%. The anilide, $(C_6H_5)_2C_4H_5SCNHC_6H_5$, melts at 118–119°.

After standing for a short time the crystals of the carbinol chloride became colored but no change in the chlorine content could be detected by analysis. No hydrogen chloride was given off when the crystals were held at 65° for twelve hours, or when a benzene solution was held at 65° for twenty-four hours.

Diphenylthienylmethyl.—The free radical was prepared by shaking benzene, bromobenzene or xylene solutions of the chloride or bromide with molecular silver at room temperature. The solutions were immediately colored red. Measurements of the amount of free radical formed by the usual oxygen absorption test[10] gave very erratic results. Depending upon the length of time the sample was left in the apparatus, absorptions ranged from 25 to 200% of the quantity theoretically required for the formation of a peroxide. Determination of the amount of silver chloride formed proved that the metal reacted completely with the halogen.

Attempts to isolate the solid free radical by usual methods gave pink crystals of melting point 157 to 162°, which gave oxygen absorptions of only 20% of the calculated value. The general behavior of this free radical was very much like that of phenylthioxanthyl.[3]

5,5′-Di-triphenylmethyl-2,2′-dithienyl, $(C_6H_5)_3CC_4H_2SC_4H_2SC(C_6H_5)_3$.—Triphenylthienylmethane was made by Weisse[11] from triphenylcarbinol and thiophene with phosphorus pentoxide as condensing agent. An attempt was made to prepare this compound from triphenylchloromethane and the Grignard reagent of iodothiophene, by analogy to the method for making tetraphenylmethane.[12] Besides quantities of triphenylmethyl peroxide and triphenylmethane, a new product was obtained, in 5 to 40% yields, which was not the methane of Weisse. The latter melts at 237°, whereas the new substance melted at 277°, after recrystallizing from ethylene dibromide.

The structure of this new product was established by its synthesis from triphenyliodothienylmethane through the Ullmann condensation, using copper-bronze.

$$2(C_6H_5)_3CC_4H_2SI + Cu \longrightarrow (C_6H_5)_3CC_4H_2SC_4H_2SC(C_6H_5)_3 + CuI_2$$

The 5,5′-positions of the triphenylmethyl groups in the thiophene rings have not been proved, but rest on the assumptions of Weisse for the constitution of the products of his phosphorus pentoxide condensations.

Two grams of triphenyliodothienylmethane was mixed with an equal volume of white sand, placed in a small flask and heated in a sulfuric acid bath to 200°. As the temperature rose further, 2 g. of copper–bronze was gradually added with stirring. When the temperature reached 250°, the flask was removed, cooled and the contents extracted with hot benzene. Concentration of the benzene extract gave a 90% yield of crystals of melting point 277°. Comparison of physical properties, solubilities and

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[10] Gomberg and Schoepfle, THIS JOURNAL, 39,1661 (1917).

[11] (a) Weisse, *Ber.*, *28*, 1537 (1895); (b) *ibid.*, *29*, 1402 (1896).

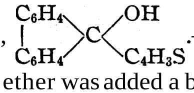
[12] Gomberg and Cone, Ber., 39, 1461 (1906).

mixed melting point proved the identity of this compound with that from the Grignard condensation. Inasmuch as the latter reaction was carried out in an atmosphere of hydrogen, the formation of the dithienyl required an oxidation at the expense of part of the reacting compounds.

The dithienyl gave no color with concd. sulfuric acid, was markedly insoluble in most solvents in the cold and was moderately soluble in hot carbon tetrachloride, ethyl acetate, naphthalene, nitrobenzene, bromoform, chloroform and benzene.

Anal. Calcd. for $C_{46}H_{34}S_2$: C, 84.88; H, 5.27; S, 9.86. Found: C, 84.85, 84.48; H, 5.62, 5.43; S, 9.81, 9.79. Mol. *wt.* Calcd.: 650. Found:[13] 670 (benzene); 668 (chloroform).

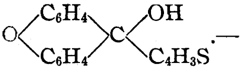
Upon bromination in boiling carbon tetrachloride solution, a dibromo compound, of melting point 287°, was obtained.

Biphenylenethienylcarbinol,  $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} OH \\ \\ C_4H_3S \end{matrix}$.—To the Grignard reagent from iodothiophene and magnesium in ether was added a benzene-ether solution of fluorenone. The light green precipitate which formed was filtered, washed and treated with ice and acetic acid. The crude carbinol was extracted with ether, washed with sodium carbonate solution and water and dried. After evaporation of the solvent, the oil was recrystallized from petroleum ether. Colorless crystals of melting point 81 to 82° were obtained. After long standing they turned green.

Anal. Calcd. for $C_{17}H_{12}OS$: C, 77.24; H, 4.58; S, 12.13. Found: C, 76.89; H, 4.62; S, 12.20.

α-Naphthylphenylthienylcarbinol $(C_{10}H_7)(C_6H_5)(C_4H_3S)COH$.—α-Naphthylphenyl ketone in ethereal solution was treated with thienylmagnesium iodide. The precipitate was washed, iced and steam distilled. The residue from the distillation was recrystallized from a mixture of ether and petroleum ether, giving colorless crystals with a melting point of 131°.

Anal. Calcd, for $C_{21}H_{16}OS$: C, 79.71; H, 5.10; S, 10.14. Found: C, 79.65; H, 4.92; S, 10.20.

Thienylxanthenol,  $O\!<\!\!\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} OH \\ C_4H_3S \end{matrix}$.—Xanthone was added in small quantities to the ether solution of thienylmagnesium iodide. The reaction was sluggish and required warming. The yellow precipitate was filtered, iced and extracted with ether. Concentration of the extract and recrystallization from ethyl acetate gave a product with melting point of 168 to 169°.

Anal. Calcd. for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.32; S, 11.44. Found: C, 72.78; H, 4.28; S, 11.42.

Thienylxanthenol chloride was made by passing dry hydrogen chloride into a solution of the carbinol in ethyl acetate. Without isolating the chloride, solutions of metal halides in ethyl acetate were added and the following double salts were obtained: $C_{17}H_{11}OSCl \cdot FeCl_3$, bronze plates, m. p. 198°; $C_{17}H_{11}OSCl \cdot HgCl_2$, small red crystals, melting with decomposition at 182 to 198°, varying with the rate of heating; $C_{17}H_{11}OSCl \cdot ZnCl_2$, red crystals, m. p. 225 to 227°.

The author wishes to express his gratitude to Professor M. Gomberg, who suggested and supervised this investigation, and to the National Aniline and Chemical Company for the aid of its Fellowship.

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[13] By ebullioscopic method of Menzies and Wright, THIS JOURNAL, 43, 2314 (1921).

Summary

Various compounds, formally derived from di-, tri- and tetraphenylmethane compounds by replacement of one phenyl group with a thienyl group, have been prepared by synthetic methods analogous to those used in preparing the corresponding phenyl compounds. The thienyl compounds were in general less stable than their phenyl analogs. The free radical, diphenylthienylmethyl, was found to possess the same instability as phenylthioxanthyl.

BUFFALO, NEW YORK

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

MONONITRO- AND DINITROTHIOPHENES. II. A STUDY OF VAPOR PRESSURES

BY V. S. BABASINIAN AND J. G. JACKSON

RECEIVED JANUARY 9, 1929 PUBLISHED JULY 5, 1949

Introductory

It is a noteworthy fact that, while the physical properties of thiophene have been made the subject of extensive study, its derivatives have received scanty attention only. Aside from sparse references to crystallographic, microscopic, optical, spectrochemical or physico-chemical studies, the literature makes no mention of the critical constants of the numerous derivatives of thiophene. This scarcity of information is probably explained by the fact that difficulty has often been experienced in the synthesis of thiophene compounds. Throughout the literature one is impressed by the glaring omission of references to percentage yields. In their extensive researches on the thiophene series, Steinkopf and co-workers[1] have recently described improved methods of preparation, but if percentage yield be taken as a measure of efficiency, the results of these workers will in numerous instances be found to leave a great deal to be desired.

During the past three years methods have been developed in this Laboratory for the quantity production of mononitro- and dinitrothiophene. The notable absence in the literature of critical data for the thiophene series has suggested a study of the vapor pressures of these nitro compounds.

Preparation and Purification of Materials.—The compounds employed in this study were synthesized by the methods outlined by one of the authors.[2] Mononitrothiophene was readily purified by steam distillation and by subsequent crystallization

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[1] (a) Steinkopf and co-workers, *Ann.*, 403, 1–72 (1914); (b) 407, 94–108 (1915); (*c*) **413**, 310–349 (1917); (d) **424**, 1–71 (1921); (e) 428, 123–163 (1922); (f) **430**, 41–161 (1923); (*g*) 437, 14–36 (1924); (h) **448**, 205–222 (1926).

[2] Babasinian, THIS JOURNAL, 50, 2749, 2751 (1928).

from petroleum ether. Repeated crystallization from this solvent produced snow-white needles which melted at 45.5°.[3]

Dinitrothiophene obtained by ordinary methods of crystallization always contains a weighable fraction of an isomer. Prolonged distillation with steam was found to remove the more volatile isomer to a great extent.[4] The residue was then freed from traces of tarry impurities by repeated crystallization from alcohol. The product was almost white and melted at 52°.[5,3a]

Method.—The apparatus employed for the vapor pressure determination was that of Smith and Menzies,[6] as shown in Fig. 1, with modifications as outlined below. Accurate temperature control was obtained by very rapid stirring of a glycerin bath A (shielded by G) by the rotary stirrer B. Temperature readings were made by means of the certified thermometer C. In order to secure greater compactness in the glass system, to eliminate leakage into the reservoirs H and I and to insure increased facility in manipulation, the apparatus of Smith and Menzies was modified as shown in Fig. 1a. In the modified form, V, I, and N remained unchanged except that I, was placed on the vacuum side of Cock N, but the reservoirs H and I were replaced by the special Cock P.[7]

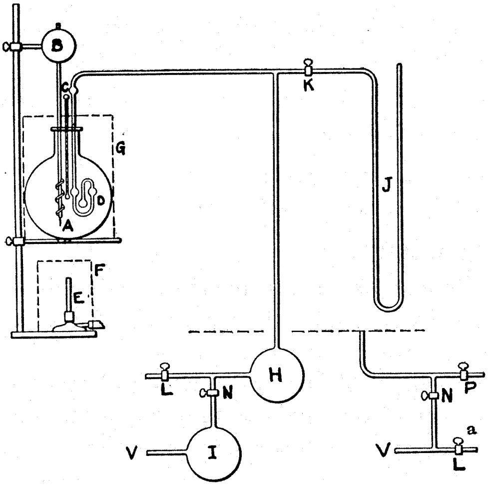

Fig. 1.—Diagram of apparatus.

Each determination required about twenty-four hours. Several readings were made at each temperature in order to insure accuracy. No decomposition was noticed in the case of mononitrothiophene at the maximum temperature of 170° employed with the compound. The liquid dinitrothiophene darkened and bore evidence of carbonization at 250°. At 256° decomposition became so rapid that it was impossible to obtain vapor pressure readings in the manometer J with any hope of accuracy. The vapor slowly attacked the mercury in the manometer at 195°. At 250° the action was more rapid, and at 260° a noticeable quantity of golden yellow flakes condensed on the surface of the mercury.

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[3] Meyer and Stadler reported 44° as the melting point of mononitrothiophene (a) *Ber.*, **17**, 2649 (1884). Steinkopf obtained a small quantity which melted at 46.5°; (b) ref. 1a, p. 18.

[4] The isomer occurs in such small quantities and is so difficult to purify that no attempt was made to produce it in quantity for vapor pressure studies.

[5] Meyer and Stadler's dinitrothiophene also melted at 52°.

[6] (a) Smith and Menzies, THIS JOURNAL, 32, 1414, 1434, 1448 (1910). This method has been employed by (b) Monroe, *Ind. Eng. Chem.*, 12, 969 (1920), on phthalic anhydride; (c) Nelson and Senseman, *ibid.*, 14, 58 (1922), on naphthalene, anthracene, phenanthrene and anthraquinone; (d) Berliner and May, THIS JOURNAL, 47, 2350 (1925); (e) *ibid.*, 48, 2630 (1926), on nitranilines and mononitrotoluenes.

[7] Cock P was specially constructed by filling the opening in the movable member of an ordinary stopcock with de Khotinsky cement, except for a small pocket at one end, in order that a minute quantity of air could be admitted when desired.

Discussion of Results

According to the Clausius–Clapeyron Equation[8]

$$L = \frac{RT^2}{p}\,\frac{dp}{dt} \tag{1}$$

where p is the corrected vapor pressure in millimeters of mercury, T the absolute temperature, L the molar latent heat of vaporization and R the gas constant. Thus the curve obtained by plotting $\log_{10} p$ against $1/T$ will be a straight line. This was done on a very large scale in the case of each substance. The result is shown in Fig. 2. The deviation of the curves from a straight line below *a* seems to indicate that the observations are not dependable in this region. In Tables I and II the vapor pressures of the substances are given at various temperatures, as ascertained from Fig. 2.

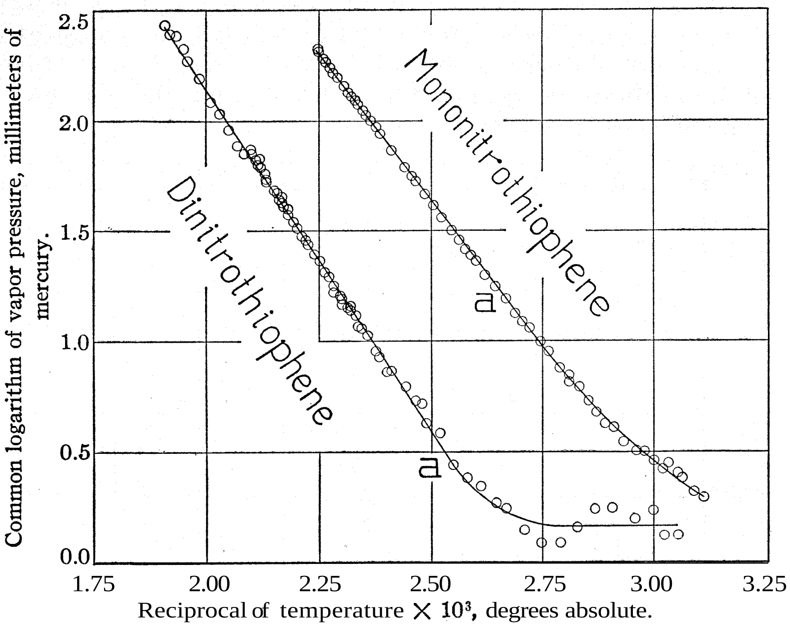

Fig. 2.

TABLE I

VAPOR PRESSURE OF MONONITROTHIOPHENE IN MM. OF MERCURY

$\log_{10} p = 8.334 - 2679.6/T$

t, °C.	105	110	115	120	125	130	135
V.p., mm.	17.7	21.9	26.9	33.0	40.1	48.7	58.5

t, °C.	140	145	150	155	160	165	170
V.p., mm.	70.3	83.9	99.8	118.6	139.6	164.8	193.6

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[8] Hugh S. Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1924, Vol. I, p. 118.

TABLE II

VAPOR PRESSURE OF DINITROTHIOPHENE IN MM. OF MERCURY

$\log_{10} p = 8.385 - 3116.1/T$

t, °C.	115	120	125	130	135	140	145	150	155	160
V.p., mm.	2.5	2.9	3.6	4.5	5.6	7.0	8.6	10.5	12.8	15.2
t, °C.	165	170	175	180	185	190	195	200	205	
V.p., mm.	18.8	22.6	27.1	32.3	38.3	45.4	53.5	62.9	73.8	
t, °C.	210	215	220	225	230	235	240	245	250	
V.p., mm.	85.9	100.0	115.6	134.3	154.2	178.2	204.2	233.9	267.3	

By extending the curve for mononitrothiophene in Fig. 2, the theoretical boiling point of that substance was found to be 218.2°, as compared with previously published results of about 224–225°.[3a] The theoretical boiling point of dinitrothiophene was found to be 293.3°, while the value given by Meyer and Stadler[3a] is 290°.

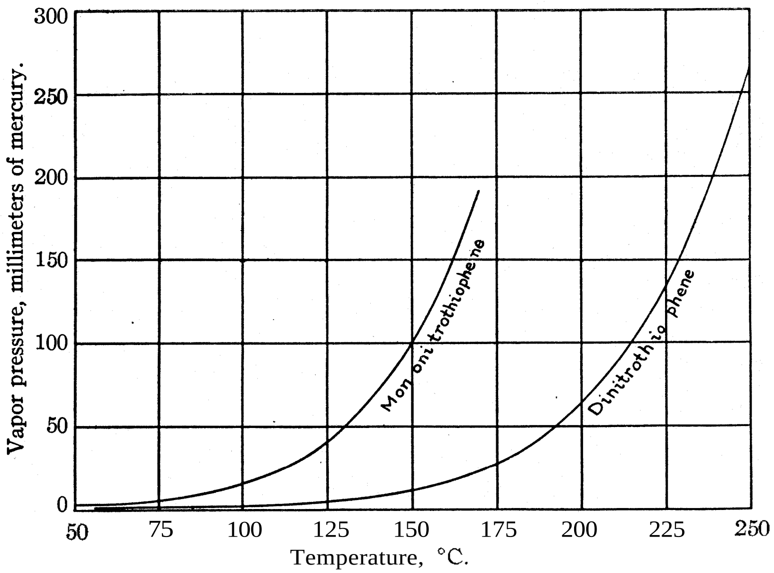

Fig. 3.

From Equation 1 the average value of L, the molar latent heat of vaporization, was found to be 12,300 cal. for mononitrothiophene above 100°, and 14,300 cal. for dinitrothiophene above 110". From these it may be determined by the method of Hildebrand[9] whether the substances are normal liquids, since

$$S = \frac{L}{RT'} \qquad (2)$$

where S is the entropy of vaporization, L the molar latent heat of vaporization and T' the temperature at which the concentration of the vapor is

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[9] Hildebrand, THIS JOURNAL, 37, 970, 974 (1915).

0.00507 mole per liter. According to the data of Hildebrand,[10] the value of S should be between **13.1** and **13.9** for a normal liquid. The values obtained for **S** were **14.7** for mononitrothiophene and 14.8 for dinitrothiophene, thus indicating that neither is a normal liquid within the range of temperature considered.

Acknowledgment

The authors desire to express their sincere acknowledgment to Professor Warren W. Ewing for numerous helpful suggestions and assistance during the progress of this study.

Summary

A study of the literature showed a marked absence of critical data for the thiophene series.

The vapor pressures of mononitro- and dinitrothiophene were measured, and their theoretical boiling points, molar latent heats of vaporization and entropies of vaporization calculated.

Mononitrothiophene showed no decomposition at the maximum temperature to which it was subjected. Dinitrothiophene was found to decompose above 250° and to attack mercury at much lower temperatures.

BETHLEHEM, PENNSYLVANIA

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

ADDITION REACTIONS OF VINYL PHENYL KETONE. I. PHENYLNITROMETHANE

BY CHARLES F. H. ALLEN AND M. PHILBRICK BRIDGESS

RECEIVED JANUARY 17, 1929 PUBLISHED JULY 5, 1929

Vinyl phenyl ketone (I) is the lowest member of the series of unsaturated phenyl ketones having a conjugated system. It should be of interest to compare the properties and reactions of the products derived from it by the addition of certain substances having active hydrogen with those obtained by the addition of the same compounds to a substituted vinyl phenyl ketone, such as benzalacetophenone (II)

$$\underset{\text{I}}{CH_2{=}CHCOC_6H_5} \qquad \underset{\text{II}}{C_6H_5CH{=}CHCOC_6H_5} \qquad \underset{\text{III}}{CH_2ClCH_2COC_6H_5}$$

Since it combines very readily with substances[1] that have an active hydrogen atom, it can be used for making saturated ketonic compounds which are unsubstituted in the beta position and which it is difficult to secure in any other manner. It seemed probable that these addition products could be converted into other substances which would be useful in connection with the study of reactions of which the mechanism is at

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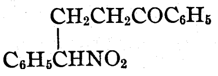
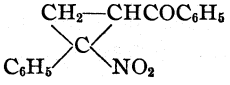
[10] **Ref.** 9, **p.** 975.

[1] Kohler, *Am. Chem. J.*, **42**, **375** (1909).

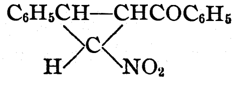
present in doubt. Thus, for example, from the addition product of phenylnitromethane (IV) it should be possible to make a nitrocyclopropane derivative (VII) isomeric with the one that is known (VIII), and a comparison of these isomers would be expected to yield valuable information on the mechanism of the peculiar rearrangements of these cyclopropane derivatives.


$C_6H_5CH(NO_2)CH_2CH_2COC_6H_5$

IV



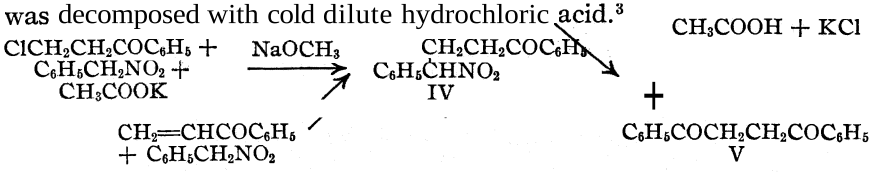
VII



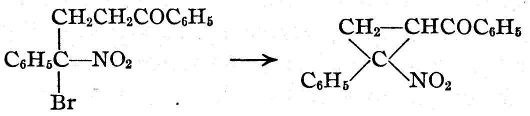
VIII

Unfortunately, the preparation of large amounts of vinyl phenyl ketone is so difficult[2] that it is not a serviceable starting material for any extensive investigations. It occurred to us that it might be possible to substitute the more readily available β-chloropropiophenone (111), and remove from it hydrogen chloride either just prior to use or in the presence of the substance to be added, thus avoiding isolation of the reactive unsaturated ketone. This procedure was, indeed, found to be possible.

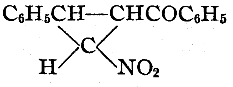
In the presence of alkaline reagents, phenylnitromethane combined with p-chloropropiophenone to give the same saturated y-nitro-ketone (IV) as was obtained with phenyl vinyl ketone. Its structure was proved by the formation of dibenzoylethane (V) when a solution of the sodium derivative was decomposed with cold dilute hydrochloric acid.[3]



On bromination in a solution of sodium methylate, followed by elimination of hydrogen bromide, a tertiary nitrocyclopropanone (VII) was produced.



VI VII



VIII

The behavior of this compound with sodium methylate was of particular interest because the previous investigations[4] showed that if a secondary

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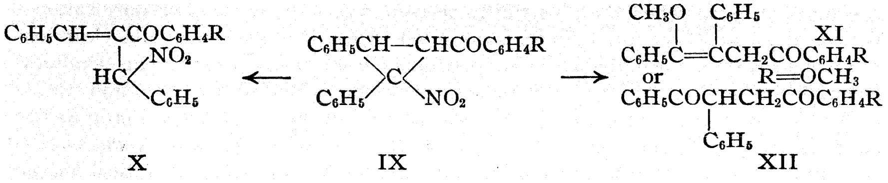
[2] (a) Van Marle and Tollens, **Ber., 36,** 1352 (1903); (b) Kohler, ref. 1, the only one to prepare any considerable quantity; (c) Beaufour, ***Bull.*** *soc. chim.* [IV] 13, 356 (1913); (d) Straus, *Ann.*, **393,** 260 (1912); 401, 142 (1913); (e) Norris and Couch, THIS JOURNAL, 42,2330 (1920); (f) Mannich, ***Ber.***, 55,356 (1922).

[3] Nef, *Ann.*, 280, 267 (1894).

[4] (a) Kohler and Engelbrecht, THIS JOURNAL, 41, 1379 (1919); (b) Kohler and Williams, *ibid.*, 41, 1644 (1919); (c) Kohler and Srinivasa Rao, *ibid.*, 41, 1697 (1919); (d) Kohler and Smith, *ibid.*, 44, 624 (1922); *(e)* Kohler and Paul Allen, *ibid.*, 50, 884 (1928).

nitro group was present (VIII), the final product was a 1,3-diketone, while with a tertiary nitro group (IX) two types of reaction occurred, one forming an ethylenic compound with the nitro group still present and the other a nitrogen-free 1,4-diketone (or its monomethyl ether).

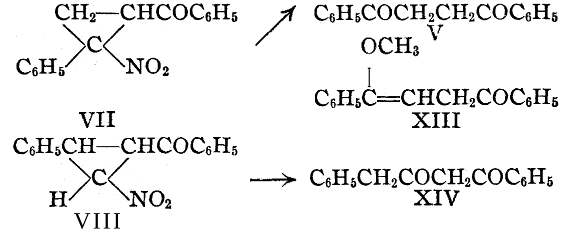


After separation of one of the two theoretically possible isomers of (VII), a lower-melting solid was deposited from the solution; this substance analyzed for an isomer, but was a constant-melting mixture undoubtedly containing some of the cyclopropane first isolated, since mixtures always gave melting points intermediate between those of this solid and the pure cyclopropane. All efforts to separate it into its constituents by fractional crystallization or change of solvents were unsuccessful.

Both this solid and the isomeric cyclopropane derivative reacted with sodium methylate, yielding dibenzoylethane (V) and its methyl ether (XIII).

The formation of dibenzoylethane can only be explained by the opening of the ring between carbon atoms 1 and 2—a new type of reaction between cyclopropane ketones and alkaline reagents. Those studied previously, chiefly by Kohler and his students, if attacked by bases, were always opened in the 1,3- or 2,3-positions. There is nothing novel about the ring being broken in different places by other reagents (*e. g.*, reducing agents have attacked all three possible bonds), but this is the first time that alkaline reagents have been found to react in the 1,2-position.

The isomeric nitrocyclopropanone (VIII)[4a] under similar conditions also opened between the carbon atoms to which the phenyl and benzoyl groups are respectively attached, and the final product is a 1,3-diketone (XIV).



Experimental

The Addition Product with Phenylnitromethane

γ-Nitro-γ-phenylbutyrophenone (IV). A.—Fifteen grams of β-chloropropiophenone[5] and 12 g. of fused potassium acetate were dissolved in 60 cc. of hot methyl

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[5] Prepared by the method of Hale and Britton, THIS JOURNAL, 41, 844 (1919).

alcohol. Then 12 g. of phenylnitromethane in 20 cc. of alcohol was added and the whole made faintly alkaline to litmus by admitting a 5% solution of sodium methylate, drop by drop. The reddish mixture was refluxed for forty minutes, then acidified with acetic acid and poured into 120 cc. of cold water. After several hours the precipitated addition product was filtered; the average yield of several preparations was 82%—this was true only when the phenylnitromethane was redistilled. For purification it was dissolved in 40 cc. of hot benzene and dried with calcium chloride; the clear solution was decanted, warmed slightly and petroleum ether added to incipient cloudiness. The addition product crystallized in clusters of needles which were filtered and washed until white with a 1:1 mixture of ether and petroleum ether. A second crop was secured by partial evaporation of the mother liquor. Further purification was eflected by a similar treatment or by recrystallization from methyl alcohol. Analytical samples prepared by either method gave the same result.

γ-Nitro-γ-phenylbutyrophenone crystallizes in bunches of needles that melt at 72°. It is very soluble in all the usual organic solvents except petroleum ether. It tends to separate as an oil from solutions containing other substances.

Anal. Calcd. for $C_{16}H_{15}O_3N$: C, 71.4; H, 5.6. Found: C, 71.3; H, 5.7.

We did not try to isolate the vinyl phenyl ketone (except in one instance, to see that it was formed) or determine the extent of its formation quantitatively. Since none of the acetate, which has previously been isolated,[1] was found at any time, the reaction between the chloro ketone and potassium acetate is probably best represented as follows

$$ClCH_2CH_2COC_6H_5 + CH_3COOK = CH_2{=}CHCOC_6H_5 + CH_3COOH + KCl$$

B.—Vinyl phenyl ketone was prepared by the method described by Mannich.[2f] The yellow oil from the steam distillation was dissolved in ether, dried over calcium chloride and the solvent evaporated in a tared flask. This residual oil was used without further purification.

To 3.8 g. of the ketone was added 10 cc. of absolute methyl alcohol; most of it immediately polymerized to a white, insoluble mass. The whole was warmed and the clear solution decanted from the polymer into a clean flask. Two grams of phenylnitromethane was added, then enough dilute sodium methylate to give an alkaline reaction to litmus, and the mixture warmed on the steam-bath for fifteen minutes. It was next acidified with acetic acid; an oil separated and crystallized on cooling. This was purified as described above and identified as the same substance by a comparison of melting points, mixed melting points and solubilities.

Proof of Structure.—One gram of the addition product was dissolved in a slight excess of sodium methylate, 10 cc. of water added and the clear solution filtered into 25 cc. of cold, dilute (1:5) hydrochloric acid. The white precipitate thus formed was filtered and recrystallized from methyl alcohol; yield, 0.7 g., or 80%. It was identified as dibenzoylethane (V) by melting point and mixed melting point with an authentic sample.[6]

Bromination.—The nitro ketone was readily brominated in sodium methylate solution, the bromine replacing the hydrogen on the y-carbon atom. Like many other compounds having a bromine atom and nitro group on the same carbon atom, this substance decomposed just above its melting point.? The reaction is not clean, but the principal product is 2,5-diphenyl-3-bromofuran.

γ-Bromo-γ-nitro-γ-phenylbutyrophenone (VI).—Ten and two-tenths grams of

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[6] Kindly supplied by Dr. R. E. Lutz.

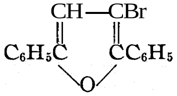
[7] Some of these compounds have been investigated by one of us; the results will appear in a subsequent paper.

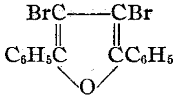
the nitro ketone was added to the sodium methylate solution prepared from 0.8 g. of sodium and 65 cc. of methyl alcohol, the whole being cooled in an ice-bath and well stirred. After ten minutes a slight excess over the theoretical amount of bromine was run in from a dropping funnel, the end of which was drawn out into a fine capillary. A white solid soon separated. The excess bromine was removed by sodium bisulfite solution, and the buff-colored precipitate filtered and thoroughly washed with water and alcohol; yield of crude solid, 94%. It was recrystallized rapidly from glacial acetic acid; prolonged heating resulted in decomposition. It formed long, fine prisms that melted at 146° with gas evolution. It is insoluble in petroleum ether, very slightly soluble in ether and the alcohols, moderately soluble in acetone, ethyl acetate and chloroform, but easily soluble in glacial acetic acid or pyridine; a solution in the latter solvent does not readily lose hydrogen bromide.

Anal. Calcd. for $C_{16}H_{14}O_3NBr$: Br, 22.7. Found: Br, 22.3.

After boiling for fifteen minutes with alcoholic sodium hydroxide and acidifying the solution, a 50% yield of dibenzoylethane resulted; the residue remained as an oil.

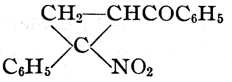
The Bromofurans,



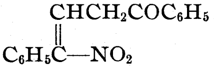


A solution of the bromonitro compound in glacial acetic acid was refluxed for an hour; oxides of nitrogen appeared in the condenser. The black solution was poured into water, the precipitated oil extracted with ether, the extract dried with calcium chloride and the solvent allowed to evaporate spontaneously. The oil left was then dissolved in methyl alcohol; on slow evaporation crystals separated; they melted at 76–77°, and on recrystallization at 77–78°. They were identified as 2,5-diphenyl-3-bromofuran by comparison with a sample at hand. A small amount of another solid was also isolated and identified as 2,5-diphenyl-3,4-dibromofuran, m. p. 88°.[6]

The Nitrocyclopropanones.—The bromo ketone loses hydrogen bromide very slowly in a boiling methyl alcoholic solution of potassium acetate, but prolonged heating gives a good yield of cyclopropane. By derivation, substances formed from (VI) by loss of hydrogen bromide could be cyclopropane derivatives (VII), ethylenic compounds (XV, XVI), or dihydrofuran derivatives (XVII), but since in all such previous instances only the cyclopropane has been formed, it would be expected here. Further, the products neither decolorize bromine nor reduce permanganate, thus excluding the ethylenic compounds (XV, XVI). Also, as furan rings are not sensitive to alkaline reagents, although the substance (XVII) could lose nitrous acid, the product expected would be the known 2,5-diphenylfuran.

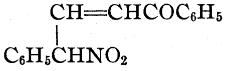


VII



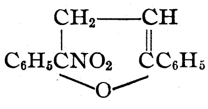
$$\begin{matrix} CHCH_2COC_6H_5 \\ \| \\ C_6H_5C—NO_2 \end{matrix}$$

XV



$$\begin{matrix} CH{=}CHCOC_6H_5 \\ | \\ C_6H_5CHNO_2 \end{matrix}$$

XVI



XVII

1-Phenyl-1-nitro-2-benzoylcyclopropane (X).—Fifteen grams of the bromo compound and an equal weight of fused potassium acetate in 75 cc. of absolute methyl alcohol was refluxed for twenty-two hours. The solution was decanted from the bulk of the potassium bromide and the solvent partially evaporated. An oil separated on cooling, but soon solidified; the crude product was filtered; yield, 90%. It was submitted to fractional crystallization, using different solvents, in an effort to isolate both isomeric forms. Ethyl acetate gave the best separation; most of the high-melting cyclopropane crystallized out first, followed by a mixture of constant melting point. Attempts to separate this into its constituents were unsuccessful. Both the pure nitrocyclopropane and the mixture crystallized in rosets, made up of fine white needles, which dissolved easily in all the usual organic solvents except petroleum ether. The pure substance melts at 131° and the mixture at 80°. The analytical samples were crystallized from methyl alcohol.

Anal. Calcd. for $C_{16}H_{13}O_3N$: C, 71.9; H, 4.9. Found: (131") C, 71.7; H, 5.0; (80°) C, 71.7; H, 5.1.

The melting points of mixtures in several proportions of the pure nitrocyclopropane and the substance of constant melting point all were above that of the latter and below that of the former. Neither solid reduces permanganate nor decolorizes bromine. They may be recrystallized unchanged from acetyl chloride. On addition to concd. sulfuric acid, a bright green color was produced and oxides of nitrogen were evolved. This reaction is to be investigated.

Action of Sodium Methylate.—Five grams of the constant-melting substance was added to 40 cc. of 5% sodium methylate solution; on warming, the solid dissolved and solid sodium nitrite separated from the brown liquid. The latter was decanted into a separatory funnel containing 100 cc. of water and enough ether added to give two layers. The ether layer was separated and the aqueous layer extracted once. The combined ethereal solutions were washed with water, followed in order by solutions of sodium bicarbonate, copper acetate, potassium carbonate and water, and then dried over calcium chloride. On evaporation, **2.4** g. of yellow oil was left; it slowly deposited dibenzoylethane. The original aqueous layer was acidified, extracted with ether and the extract treated similarly. On evaporation it left 1.7 g. of an oil that deposited more dibenzoylethane during the course of a month. The total yield of diketone was 70%. Nothing was obtained from any of the solutions used to wash the ethereal extracts. When the operation was interrupted after five minutes, the first ether extract deposited high-melting nitrocyclopropane as well as dibenzoylethane.

The cyclopropane, m. p. 131°, behaved similarly, on the same treatment; 4.1 *g* of oil was obtained. During the course of three weeks it slowly deposited **55%** of the theoretical amount of dibenzoylethane and 10% of the theoretical amount of the monomethyl ether of that diketone (XIII). This was a very sensitive substance, difficult to recrystallize without hydrolysis to dibenzoylethane. It is very soluble in all the usual solvents; methyl alcohol gave fine, white needles, m. p. 72".

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 81.0; H, 6.4. Found: C, 81.1; H, **6.3.**

On cautious oxidation by permanganate the odor of methyl benzoate could **be** detected; benzoic acid was also identified.

A small portion of the oil was oxidized by permanganate; no benzaldehyde could be detected; the sole solid product was benzoic acid. **A** second portion failed to **give** a solid when treated with semicarbazide in the usual way.

This tertiary nitrocyclopropane is relatively inactive with hydrogen bromide. The mixed solid is turned into the high-melting form (131°) which does not react.

This work has been assisted by a generous grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

We are indebted to Professor E. P. Kohler for valuable criticism in **the** preparation of this paper.

Summary

1. It has been shown that β-chloropropiophenone can be used in place of vinyl phenyl ketone in addition reactions. With phenylnitromethane the same γ-nitro ketone is obtained from both substances.

2. The nitro ketone is easily brominated in the gamma position; the bromo ketone is unstable to heat. Hydrogen bromide is eliminated by the use of potassium acetate, and the product is a tertiary nitrocyclopropanone.

3. Sodium methylate reacts with this cyclic nitro compound in such a way that the ultimate product is dibenzoylethane.

TUFTS COLLEGE, MASSACHUSETTS

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

TRIARYLMETHYL CARBONATES. CATALYTIC DECOMPOSITION IN THE PRESENCE OF COPPER

BY J. O. HALFORD

RECEIVED JANUARY 31, 1929 PUBLISHED JULY 5, 1929

Triphenylmethyl carbonate has been recorded by Gomberg[1] as an intermediate in the preparation of triphenylmethyl oxide. The carbonate was formed by the action of silver carbonate on triphenylchloromethane in benzene

$$2(C_6H_5)_3CCl + Ag_2CO_3 = [(C_6H_5)_3C]_2CO_3 + 2AgCl \qquad (1)$$

A solution of triphenylmethyl carbonate in boiling xylene produced triphenylmethyl oxide and carbon dioxide under the catalytic influence of finely-divided copper.

$$[(C_6H_5)_3C]_2CO_3 \longrightarrow CO_2 + [(C_6H_5)_3C]_2O \qquad (2)$$

This reaction, similar to the thermal decomposition of metallic carbonates, is consistent with the general properties of the triarylmethyls, whose salts with strong acids, particularly the halides, show many of the reactions of metallic salts. If the analogy is complete, Equation *2* should represent a general reaction of the triarylmethyl carbonates and should be reversible.

With this in mind, three other carbonates, those of diphenyl-α-naphthylmethyl, p-tolyldiphenylmethyl and phenylbiphenylenemethyl, have been prepared and their behavior in the presence of copper powder studied. Although p-tolyldiphenylmethyl carbonate and diphenyl-α-naphthylmethyl carbonate are decomposed catalytically by copper, the oxides have not been obtained in appreciable quantity and it must be concluded that Reaction 2 is not general, but that the catalytic effect of copper is common to the triarylmethyl carbonates. The decomposition of triphenylmethyl carbonate has not been reversed.

Further, the occurrence of a slow catalytic decomposition presents an opportunity to study the mechanism through the interpretation of the rate of reaction. This has been done for the decomposition of triphenylmethyl carbonate.

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[1] Gomberg, THIS JOURNAL, 35, 200 (1913).

Triphenylmethyl Carbonate.—Ten grams of triphenylchloromethane in 50 cc. of dry benzene was shaken with two to three times the theoretical amount of silver carbonate for twenty-four hours. The silver carbonate had been dried at 140° in a stream of carbon dioxide and analyzed as 99.7% pure. The benzene solution was heated to boiling, filtered and the residue extracted with 50 cc. of boiling benzene. The volume was reduced to 30 cc. at low pressure on the steam-bath. The carbonate crystallized rapidly and was light yellow in color. One recrystallization produced white crystals containing one molecule of benzene of crystallization. The yield is 60–80%; m. p. 200–201° with carbon dioxide evolution.

Anal. The carbon dioxide evolved by heating to 200° was weighed. Calcd. for $C_{45}H_{36}O_3$: CO_2, 7.05. Found: CO_2, 7.00, 7.03.

Part of the benzene was removed by heating for several hours in a vacuum at 90°, the rest by recrystallization from xylene and washing with dry ether; m. p. 208–209° with carbon dioxide evolution.

Anal. Calcd. for $C_{39}H_{30}O_3$: CO_2, 8.06. Found: CO_2, 7.98, 8.12. The first measurement (7.98) was obtained by heating the dry solid, the second (8.12) by titrating the carbonate produced by alkaline hydrolysis. *Mol. wt.* in benzene, calcd., 546. Found: 523, 560, 531, 531; average 536. The solubility in hot benzene is about 55 g. per 100 cc.; in cold benzene, 2 g. per 100 cc.; in hot acetone, 5 g. per 100 cc.; in hot ethyl acetate, 20 g. per 100 cc. Long standing in ethyl acetate slowly produces triphenylcarbinol.

Triphenylmethyl Oxide.—A sample of triphenylmethyl oxide was obtained by the action of mercuric oxide on triphenylchloromethane;~ m. p. 232–233°. Five grams of triphenylmethyl carbonate was heated in boiling xylene for two hours. It crystallized unchanged. The experiment was repeated with the addition of a small quantity of copper powder. The resulting crystals melting at 235–236° were identified with triphenylmethyl oxide by a mixed melting point of 233–234°; yield, 95%. Recrystallization from xylene raised the melting point to 237–238°.

Diphenyl-a-naphthylmethyl Carbonate.—In the preparation of this substance, it is desirable, because of its low solubility, to use 10 cc. of benzene for each gram of diphenyl-a-naphthylchloromethane. The solution of the product in benzene was evaporated under reduced pressure to a thick sirup and crystallized by the addition of ether. Crystallization of the crude carbonate required twenty-four to forty-eight hours. The product at first obtained was dark yellow and contained 20 to 40% of impurities; yield 40–60%. Recrystallization from boiling xylene (20 cc. per gram) produced a white powder melting with carbon dioxide evolution at 228–230°.

Anal. Calcd. for $C_{47}H_{36}O_3$: CO_2, 6.8 Found: CO_2, 6.2, 6.6. Mol. *wt.* in benzene, calcd., 648. Found: 638, 639.

A solution of diphenyl-a-naphthylmethyl carbonate in xylene was boiled for an hour without appreciable carbon dioxide evolution. The addition of copper powder effected complete decomposition in thirty to forty-five minutes. However, no substance was successfully crystallized from the product, showing that diphenyl-α-naphthylmethyl oxide is probably unstable under the conditions of the experiment.

Diphenyl-a-naphthylchloromethane in benzene was kept in contact with mercuric oxide for several days. A 50% yield of diphenyl-a-naphthylcarbinol was obtained. The remainder was precipitated as a gum by petroleum ether and was not successfully crystallized. The occurrence of the carbinol in this quantity suggests the abstraction of hydrogen chloride and subsequent decomposition of half the material, accompanied by hydrolysis of the other half.

***p*-Tolyldiphenylmethyl** Carbonate.—This compound is the most soluble in benzene and xylene of the carbonates prepared. It was obtained as a white powder by adding ether to the oily residue left after removal of the benzene used in the preparation. Four or five cc. of xylene per gram is sufficient for recrystallization; yield, 40–50%. The melting point is 193–195° with carbon dioxide evolution. For analysis the sample was refluxed in a solution of 0.1 *N* sodium hydroxide, barium chloride was added, and excess alkali titrated to phenolphthalein.

Anal. Calcd. for $C_{41}H_{34}O_3$: CO_2, 7.66. Found: CO_2, 7.40, 7.45. *Mol. wt.* in benzene, calcd., 574. Found: 556, 568.

***p*-Tolyldiphenylmethyl Oxide.**—The use of xylene in recrystallizing *p*-tolyldiphenylmethyl carbonate shows its stability at 140°. The introduction of powdered copper into the solution in boiling xylene or toluene resulted in rapid carbon dioxide evolution. A small amount of white powder melting at 180–185° was separated. The reaction of p-tolyldiphenylchloromethane with mercuric oxide produced a 10% yield of white material melting at 205–207°. This latter must be the oxide since it has a high melting point and is readily converted to the carbinol by hydrochloric acid. One part of this substance was mixed with three parts of the material melting at 180–185° and a mixed melting point of 190–195° was obtained, showing that a small quantity of the oxide was produced by decomposition of the carbonate in the presence of copper. Evidently the p-tolyldiphenylmethyl compounds enter, to some extent, into the same reactions as the triphenylmethyl compounds.

The residue from the *p*-tolyldiphenylmethyl oxide preparation by the mercuric oxide method was a yellow oil from which nothing was crystallized. This result is similar to that of Schlenk and Meyer,[2] who attempted to prepare diphenylquinomethane from p-tolyldiphenylchloromethane and pyridine but obtained only a yellow oil from which nothing was crystallized. In this case mercuric oxide may have produced the same result as pyridine.

Phenylbiphenylenemethyl Carbonate.—A solution of phenylbiphenylenechloromethane in benzene slowly turned dark red when kept in contact with silver carbonate. A 10% yield of pink crystalline material was obtained. White crystals melting with carbon dioxide evolution at 218–220° were separated by recrystallization from xylene. Heating in boiling xylene with or without copper for four to five hours failed to produce carbon dioxide evolution. The compound was decomposed by boiling in mesitylene over copper but phenylbiphenylenemethyl oxide was not obtained. This behavior is not surprising in view of the high stability and generally sluggish reactions of the phenylbiphenylenemethyl compounds.

Rate of Carbon Dioxide Evolution by Triphenylmethyl Carbonate

The mechanism of carbon dioxide evolution from triphenylmethyl carbonate in boiling xylene under the influence of powdered copper was studied through the rate of evolution of the gas. Rate measurements on the other carbonates were not made because their decomposition was complicated by side reactions. The triarylmethyl oxide was produced quantitatively only from triphenylmethyl carbonate.

The carbon dioxide evolved in the flask A was carried through the reflux condenser into the receiver B by a stream of dry nitrogen. The nitrogen was passed through soda lime and dried with phosphoric anhydride before entering the apparatus. Xylene was distilled in a small apparatus which

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[2] Schlenk and Meyer, *Ber.*, 52, 16 (1919).

had been dried in an oven at 110°. The flask **A and** the reflux condenser were dried in the oven before use. Very small amounts of water interfered by hydrolysis of the carbonate. For example, calcium chloride instead of phosphoric anhydride let through enough water in an hour for complete hydrolysis of a gram of the carbonate. The receiver B contained a known amount of standard barium hydroxide whose concentration as a function of time was measured by means of the conductivity cell C. The pipet cell allowed sampling at definite time intervals with sufficient time for measurement. The outlets of the flask and cell were protected by soda lime tubes D. The temperature in the reaction flask was 139° during all the runs and the barium hydroxide in the receiving flask was kept at 25°. At the end of each run the triphenylmethyl oxide produced was separated and in each case was found to represent a 90–95% yield without taking into account the solubility in xylene. The xylene solution was made up each time in the same concentration and approximately the same quantity, **1** g. of carbonate to 24 g. of xylene. The resistance of the barium hydroxide as a function of concentration was found to be expressed accurately by the equation, log $CR^{1.0801}$ = **0.61584.** The

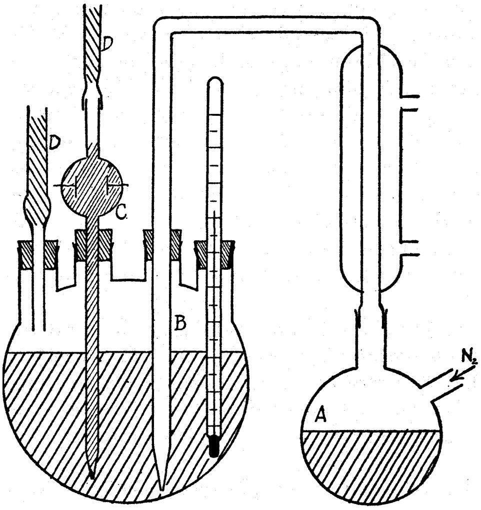

Fig. 1.

TABLE I

RATE OF EVOLUTION OF CARBON DIOXIDE AT 139° BY TRIPHENYLMETHYL CARBONATE IN XYLENE

Carbonate, 0.8827 **g.; copper** 1.1581 **g.; xylene** 22.0 **g.**

Time, minutes	R, ohms	Concn. $Ba(OH)_2$ X 10^2 moles/liter	CO_2 X 10^6, equivalents	K
0	57.6	5165	000	...
3	62.0	4778	387	0.092
6	62.3	4753	412	.046
9	62.8	4704	461	,038
14	66.0	4355	810	.0N
20	69.4	4227	938	.044
25	72.6	4036	1129	.047
30	74.3	3945	1220	.047
40	76.2	2828	1337	.048
50	79.0	3681	1484	.0N
60	79.9	3641	1524	.048
70	81.3	3573	1592	.060

range of concentration was 0.1 to 0.025 *M*. The results of a typical run are given in Table I. The last column gives the unimolecular rate constant in reciprocal minutes. The volume of barium hydroxide was 200 cc.

With a rapidly boiling solution no interference by rate of diffusion was encountered. Some distortion of the rate curve might be expected during the first and more rapid part of the reaction due to lag in carrying over the carbon dioxide. This, however, was negligible since changes of the rate of flow of nitrogen during the reaction were without effect on the results.

In Table II the effect of the amount of copper surface is summarized. The first row gives the weight of copper per gram of triphenylmethyl carbonate; the second, the unimolecular rate constant. The solution in each case contained 1 g. of carbonate in 24 g. of xylene.

TABLE II

EFFECT OF THE EXTENT OF COPPER SURFACE ON THE RATE OF CARBON DIOXIDE EVOLUTION

Cu, grams	3.15	1.57	0.90	0.75	0.38
K	0.047	0.046	0.032	0.025	0.028

Although the fourth and fifth points are in reverse order, it is evident that doubling the copper surface produced only a small increase in the rate.

A series of qualitative experiments failed to discover any substance other than copper powder which would catalyze the reaction. Freshly reduced nickel, platinum and cadmium were without effect. With the possibility of intermediate metallic carbonate formation in mind, stannic oxide, mercuric oxide and cupric oxide were tried. The last two are significant, mercuric oxide because of its use in preparing the triarylmethyl oxides and cupric oxide because of the possibility of an oxide film on the surface of the catalyst. Although negative results are not necessarily significant in catalysis, the reaction is probably the result of a specific property of copper. The reaction was carried out with two samples of copper from different sources, although all rate measurements were made with the same sample to obtain a uniform surface.

Mechanism of the Reaction.—A catalytic reaction at a solid–liquid interface should be unimolecular[3] if it is governed by a rate of diffusion or by adsorption covering only a small fraction of the active surface at any time. In either case the amount reacting in unit time at a given concentration should be proportional to the surface, or nearly so, if the reaction causes adsorption to lag behind equilibrium. Since the rate constant is defined as the quantity reacting in unit time at unit concentration, it follows that the constant should increase in direct proportion to the surface. It must be concluded, then, that in the reaction studied the catalytic

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[3] Taylor, "Physical Chemistry," D. Van Nostrand Company, Inc., New York, 1924, p. 953.

effect cannot be explained in terms of adsorption covering a small fraction of the active surface. However, if the catalyst is able to produce and maintain an equilibrium concentration of active molecules in the solution, rather than on the surface, the results are explained. If equilibrium were maintained by the catalyst, the constant would be independent of the extent of the surface; but if it is assumed that increasing the surface decreases the lag behind equilibrium, a large increase in the active surface should be attended by a small increase in the rate constant. The experimental results give no indication of the nature of such an intermediate but, since the yield of triphenylmethyl oxide is almost quantitative, it is probably a tautomer or active form of the carbonate itself.

Levi and Haardt[4] obtained a similar result in a measurement of the effect of the surface area of platinum on the rate of decomposition of hydrogen peroxide. Vavon[5] found that the rate of hydrogenation of nitrobenzene in alcohol increased rapidly with the weight of catalyst employed.

Summary

Triphenylmethyl carbonate, diphenyl-α-naphthylmethyl carbonate, *p*-tolyldiphenylmethyl carbonate and phenylbiphenylenemethyl carbonate have been prepared.

The evolution of carbon dioxide in boiling xylene from the first three of the carbonates mentioned has been shown to be catalyzed by copper powder. Phenylbiphenylenemethyl carbonate was not affected by copper, triphenylmethyl carbonate broke down quantitatively to triphenylmethyl oxide and carbon dioxide. Diphenyl-a-naphthylmethyl carbonate decomposed without producing the oxide, and a small quantity of *p*-tolyldiphenylmethyl oxide was obtained from *p*-tolyldiphenylmethyl carbonate.

p-Tolyldiphenylmethyl oxide was also prepared in small quantity from mercuric oxide and *p*-tolyldiphenylchloromethane.

The rate of evolution of carbon dioxide from triphenylmethyl carbonate catalyzed by copper in boiling xylene was measured as a function of the extent of copper surface. The rate constant was unimolecular and the effect of extent of surface precluded explanation in terms of adsorption. An alternative explanation has been given.

ANN ARBOR, MICHIGAN

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[4] Levi and Haardt, *Gazz. chim. ital.*, 56,424 (1926).

[5] Vavon, *Bull. soc. chim.*, **41,** 1253 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

CATALYTIC REDUCTION OF ALPHA-DIKETONES AND THEIR DERIVATIVES

BY JOHANNES S. BUCK AND SANFORD S. JENKINS[1]

RECEIVED FEBRUARY 23, 1929 PUBLISHED JULY 5, 1929

In order to obtain certain derivatives of a-diketones the authors investigated the catalytic reduction of benzils. The usual methods given in the literature are difficult and give poor yields. Five benzils were selected as starting materials: benzil made by the oxidation of benzoin with nitric acid;[2] anisil derived from anisoin after the method of Bösler;[3] piperil made from piperoin by oxidation with Fehling's solution;[4] veratril, obtained by oxidizing the crude reaction product of veratric aldehyde and alcoholic potassium cyanide;[5] and, finally, furil, prepared by oxidizing furoin in air.[6]

The catalytic reduction method of Adams[7] was selected, but as it was desired to work with quantities of the order of 0.005-0.01 mole, the apparatus was modified to this end. A second gage was inserted in the line between the reservoir and the bottle (Burgess–Parr Company's apparatus) as shown in the sketch. After the bottle was filled with hydrogen, it was cut off from the reservoir by means of the needle-valve. Under these conditions it functions as its own reservoir, the pressure in the bottle being read on the second gage. Since the capacity of the bottle is about 0.05 that of the tank, a correspondingly small amount of material will give about the same drop in pressure.

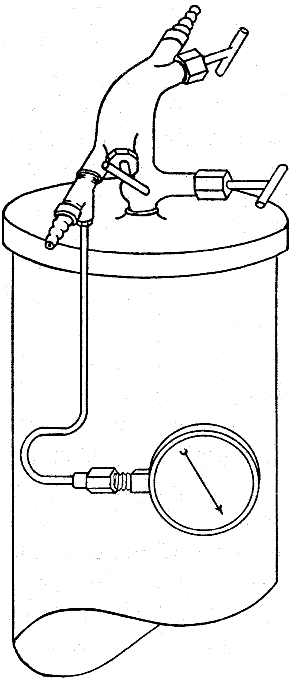

Fig. 1.

It is essential to guard carefully against leaks and to control the temperature within narrow limits. The authors find that benzoin is a very satisfactory material for calibrating the apparatus for one molecule of hydrogen, and benzil for two

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[1] Presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Duke University.

[2] Zinin, ***Ann.,*** 34, 188 (1840).

[3] Bosler, ***Ber.,*** 14, 327 (1871).

[4] Biltz and Wienands, ***Ann.,*** 308, 11 (1899).

[5] Fritsch, *ibid.,* 329, 53 (1903); Vanzetti, *Gazz. chim. ital.,* 57, 162 (1927).

[6] Fischer, *Ann.,* 211, 221 (1882).

[7] Voorhees and Adams, THIS JOURNAL, 44, 1397 (1922).

molecules of hydrogen. Heating the solution very often greatly speeds up the reduction and facilitates the solution of difficultly soluble compounds. The bottle was therefore heated by means of a thin copper cylinder, insulated and wound with resistance wire, current being supplied by a step-down transformer and controlled by a rheostat. It is necessary to calibrate the apparatus for each temperature and the temperature must be held sensibly constant throughout the run.

Benzil is readily reduced to benzoin and to hydrobenzoin. Usually an almost pure product was obtained after one recrystallization. When reduction was carried to completion the hydrobenzoin was obtained practically pure. The following equations represent the reaction

$$\mathrm{RCOCOR + H_2 = RCHOHCOR}$$
$$\mathrm{RCOCOR + 2H_2 = RCHOHCHOHR}$$

The solvent has an important effect on the reduction. Thus anisil reduces best in ethyl acetate, while piperil could only be reduced in pyridine. After many attempts under different conditions the authors failed to reduce veratril, but work is being continued on this compound. Furil readily takes up one molecule of hydrogen, but the action was not investigated beyond this stage as it has been dealt with by Adams.[8]

A number of attempts to dehydrate the hydro compounds to the desoxy compounds by the use of acetic and hydrochloric acids were made. In the case of hydro-anisoin a good yield of desoxyanisoin was obtained, but from hydropiperoin a compound of melting point 114°, not identical with desoxypiperoin, was obtained but not further examined. Hydrobenzoin is known to dehydrate to an anhydride and diphenylacetaldehyde. One case of similar dehydration using sulfuric acid, (hydro-anisoin and isohydro-anisoin)[9] is recorded in the literature. Iso compounds, however, were never obtained in the present research. The desoxy compounds were prepared for this work by reducing the corresponding benzoins by means of tin and alcoholic hydrochloric acid.[10] Desoxybenzoin readily reduced to toluylene hydrate. Desoxyanisoin formed di-p-methoxytoluylene hydrate, and desoxypiperoin reduced with great difficulty to form di-*p*-methylenedioxytoluylene hydrate. Twenty-four runs were made on the desoxypiperoin using various solvents and otherwise modifying conditions; only one run gave the required product in satisfactory yield. The equation $\mathrm{RCH_2COR + H_2 = RCH_2CHOHR}$ represents the process. The toluylene hydrates readily lose water under the action of a mixture of acetic acid and hydrochloric acid to form the corresponding stilbenes, $\mathrm{RCH_2CHOHR = H_2O + RCH{=}CHR}$. Stilbenes so obtained are reduced more or less readily to form the corresponding diphenylethanes.

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[8] Kaufmann and Adams, THIS JOURNAL, 45,3029 (1923).

[9] Rossel, *Ann.*, 151, 42 **(1869).**

[10] I. Allen, private communication.

It will be seen that in one case the complete series of compounds from anisil to di-p-methoxydiphenylethane can be produced catalytically (acid or platinum oxide) in excellent yield.

The following scheme represents the process (anisil as example). Benzil and piperil are similar, but lack the stage *hydro* to *desoxy compound.*

$$\underset{\text{Anisil}}{\mathrm{CH_3OC_6H_4COCOC_6H_4OCH_3}} \xrightarrow{\mathrm{H_2}} \underset{\text{Anisoin}}{\mathrm{CH_3OC_6H_4COCHOHC_6H_4OCH_3}} \xrightarrow{\mathrm{H_2}}$$

$$\underset{\text{Hydro-anisoin}}{\mathrm{CH_3OC_6H_4CHOHCHOHC_6H_4OCH_3}} \xrightarrow[\mathrm{HAc}]{\mathrm{HCl}} \underset{\text{Desoxyanisoin}}{\mathrm{CH_3OC_6H_4COCH_2C_6H_4OCH_3}} \xrightarrow{\mathrm{H_2}}$$

$$\underset{\text{Dimethoxytoluylene hydrate}}{\mathrm{CH_3OC_6H_4CHOHCH_2C_6H_4OCH_3}} \xrightarrow[\mathrm{HAc}]{\mathrm{HCl}} \underset{\text{Dimethoxystilbene}}{\mathrm{CH_3OC_6H_4CH{=}CHC_6H_4OCH_3}} \xrightarrow{\mathrm{H_2}}$$

$$\underset{\text{Dimethoxydiphenylethane}}{\mathrm{CH_3OC_6H_4CH_2CH_2C_6H_4OCH_3}}$$

The yields obtained in the foregoing reactions are excellent and would be practically quantitative if carried out on a larger scale. Compared with the usual methods of reduction (amalgam, tin and hydrochloric acid, etc.), the catalytic method is much superior, where applicable. It is interesting to note that many compounds usually described as yellow are obtained pure white by the catalytic method.

Experimental

In the following reductions 0.01 mole of substance, 50 cc. of solvent and 0.05 g. of platinum oxide were used. The product was usually identified by a mixed melting-point determination and comparison with an authentic specimen. The melting points of the crude products were usually within one or two degrees of the melting points given in the literature, indicating a high state of purity. Unless otherwise stated 0.01 mole of material was used for the reduction. The yields may be regarded as minimal in view of the small amounts of material used. For convenience the results are tabulated.

TABLE I

TABULATED RESULTS

Starting material	Product	Best solvent	Temp., °C.	Yield, %	M. p. of product, °C.
Benzil	Benzoin	Alcohol	Room	93	134
Anisil	Anisoin	Et. ac.	60	90	109–110
Piperil	Piperoin	Pyridine	60	87	118–120
Furil	Furoin ·	Alcohol	Room	86	135
Veratril	(Failed to reduce)				
Benzil	Hydrobenzoin	Alcohol	Room	90	134
Anisil	Hydro-anisoin	Et. ac.	60	88	168–170
Piperil	Hydropiperoin	Pyridine	60	80	200–202
Benzoin	Hydrobenzoin	Alcohol	60	90	134
Anisoin	Hydro-anisoin	Alcohol	60	89	168–170
Piperoin	Hydropiperoin	Alcohol	60	88	200–202

TABLE I *(Concluded)*

Starting material	Product	Rest solvent	Temp., °C.	Yield, %	M. p. of product, °C.
Desoxybenzoin	Toluylene hydrate	Alcohol	Room	85	63
Desoxyanisoin	Di-*p*-methoxytoluylene hydrate	Acetic acid	Room	85	110.4
Desoxypiperoin	Di-p-methylenedioxytoluylene hydrate	Pyridine	Room	97	154–155
Stilbene	Diphenylethane	Alcohol	Room	86	53
Di-*p*-methoxystilbene	Di-p-methoxydiphenylethane	Et ac.	60	91	125
Di-*p*-methylenedioxystilbene	Di-*p*-methylenedioxydiphenylethane	Acetic acid	60	81	138

Desoxybenzoin, desoxyanisoin and desoxypiperoin (the latter not previously described) were produced by the reduction of the corresponding benzoins with tin and alcoholic hydrochloric acid. Desoxyanisoin may also be prepared by the action of acetic and hydrochloric acids on hydro-anisoin. Desoxypiperoin forms white crystals melting at 114.5° when crystallized from acetic acid. It is sparingly soluble in alcohol and moderately soluble in acetic acid.

Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.61; H, 4.24. Found: C, 67.48; H, 4.40.

Di-p-methoxytoluylene hydrate was found to melt at 110.4°. It forms white diamond-shaped crystals.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.49; H, 6.97. Found: C, 74.32; H, 6.81.

Wiechell[11] obtained this compound in another way and reports the melting point as 170". As a check, the authors reduced desoxyanisoin with sodium amalgam and acetic acid and found the same melting point of 110". Their specimen, prepared catalytically, gave dimethoxystilbene in 90% yield when heated with acetic and hydrochloric acids.

Di-p-methylenedioxytoluylene hydrate was obtained only once out of 24 runs, and then in a yield of 97%. The compound forms white crystals from alcohol and melts at 154–155°.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.13; H, 4.89. Found: C, 66.95; H, 5.09.

The same compound was obtained in moderate yield by the reduction of desoxypiperoin with sodium amalgam and acetic acid. Prepared by either method, it was convertible into di-p-methylenedioxystilbene in 90% yield.

The stilbenes listed were obtained in 85–90% yield by heating the corresponding toluylene hydrates for ten minutes with a mixture of 80% acetic acid and 20% concentrated hydrochloric acid.

Summary

1. Benzoins are readily produced from benzils by catalytic reduction.
2. Hydrobenzoins are similarly produced from benzils or benzoins.
3. Desoxybenzoins reduce to toluylene hydrates.
4. Stilbenes, conveniently prepared by dehydrating the toluylene hydrates, give on reduction diphenylethanes.
5. Veratril failed to reduce.
6. Desoxypiperoin reduced once out of 24 trials.

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[11] Wiechell, *Ann.*, 279, 340 (1894).

7. The catalytic method, when applicable, gives excellent yields and is superior to other methods.
8. A convenient method for reducing 0.01 to 0.0025 mole is described.
9. Benzoin is recommended as a standard for calibrating the apparatus for one mole of hydrogen and benzil for two moles.
10. The complete series of reduction products of anisoin may be prepared catalytically.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE PREPARATION OF ALLOMUCIC ACID AND CERTAIN OF ITS DERIVATIVES

BY C. L. BUTLER AND LEONARD H. CRETCHER

RECEIVED MARCH 1, 1929 PUBLISHED JULY 5, 1929

While engaged in the investigation of certain sugar acids, it was desired to prepare allomucic acid in comparatively large amounts. This is one of the less common dibasic acids in the sugar group and but few of its derivatives have been described. The only published method of preparation is that of Fischer,[1] who obtained the acid by epimerization of mucic acid with excess of pyridine at 140°. The yield was 14%.

The present authors have been able to prepare pure allomucic acid from mucic acid in yield of 33%. This was accomplished under the conditions of epimerization previously employed in this Laboratory for the preparation of d-talonic acid from d-galactonic acid.[2]

It was shown by Fischer[1] that allomucic acid is partially converted into a monolactone on boiling or evaporation of a water solution. Fischer did not isolate this lactone and we were not able to prepare it in crystalline form. A solution of the lactone was used in the present work for the preparation of the mono-amide.

Diethyl allomucate was prepared by the method employed by Malaguti[3] for the esterification of mucic acid, namely, the use of a comparatively large amount of concd. sulfuric acid and alcohol. The yield was 42% of the theoretical. It was found that it was also possible to esterify with alcohol containing 1% of hydrochloric acid. This method gives a better yield (58%) of ester and is somewhat simpler in manipulation. The ester was easily converted into the diamide by addition of concd. ammonia water.

It was shown by Kiliani[4] that *l*-mannosaccharic dilactone reduces

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[1] Fischer, *Ber.*, 24, 2136 *(1891).*

[2] Hedenburg and Cretcher, THIS JOURNAL, 49, **478** (1927).

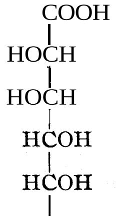
[3] Malaguti, *Ann. chim. phys.*, *[2]* **63,** 86 (1836).

[4] Kiliani, *Ber.*, 20, 339, 2710 (1887).

Fehling's solution and that in alkaline solution it rapidly becomes yellow when heated. Very recently,[5] he again studied the properties of this lactone and made the surprising discovery that it adds hydrogen cyanide to give a compound which can be hydrolyzed to a tricarboxylic acid.

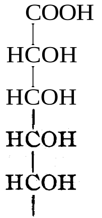
Fischer[6] has reported that d-mannosaccharic dilactone also reduces Fehling's solution. This fact has been confirmed in our laboratory.

Mannosaccharic acid, so far as the authors have been able to learn, is the only dibasic sugar acid possessing these properties. Inspection of the formulas of mannosaccharic and allomucic acids shows that they are



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{COOH}\end{array}$$

Mannosaccharic acid



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{COOH}\end{array}$$

Allomucic acid

similar in that the two hydroxyl groups adjacent to each of the carboxyl groups are in the cisposition.

This is not true of any other of the dibasic sugar acids. If this configuration is responsible in any way for the properties of mannosaccharic acid, it might be expected that similar properties would be observed in the case of allomucic acid. However, tests failed to confirm this prediction. Allomucic acid was found to be non-reducing, both when tested with Fehling's reagent immediately after solution and when tested after boiling an aqueous solution for one-half hour to convert to lactone. It remained colorless when boiled with 10% sodium hydroxide. Moreover, while mannosaccharic acid readily forms the dilactone, allomucic acid apparently forms only a monolactone under ordinary conditions.

Experimental

Preparation of Allomucic Acid.—One hundred g. of mucic acid, 1000 cc. of water and 100 g. of pyridine were placed in a 2-liter round-bottomed flask and the mixture was heated to boiling. The flask was then tightly closed with a rubber stopper which was wired in position. The flask was wrapped with cloth and heated for 115 hours on a steam-bath. One hundred and fifty g. of crystallized barium hydroxide dissolved in hot water was then added. This precipitated the barium salts of mucic and allomucic acids. The mixture was vacuum distilled until practically all of the pyridine was removed. After cooling, the crude barium salt was filtered off, washed with water and dried. The yield was 160 g. The salt was suspended in 1500 cc. of hot water and the calculated amount of sulfuric acid (based on the amount of barium found by analysis) was added. The mixture was heated, with stirring, on a steam-bath for two hours.

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[5] Kiliani, Ber., 61, 1155 (1928).

[6] Fischer, *ibid.*, 24, 539 (1891).

It was then filtered and the residue, which consisted of a mixture of barium sulfate and unchanged mucic acid, removed by filtration and washed with a little hot water. After treatment with decolorizing carbon, the filtrate was obtained as a pale yellow liquid. It was then concentrated under reduced pressure to 500 cc. and allowed to stand overnight in the ice box. The mucic acid which crystallized was removed by filtration. The filtrate was evaporated to half its volume under reduced pressure, at about 60°, and allowed to stand in the ice box overnight. The crystalline material, which still contained a small amount of mucic acid, was filtered off and treated with ten times its weight of boiling water. The mixture was filtered hot. Crude allomucic acid separated from the filtrate on cooling. The main bulk of mother liquor was again evaporated to half its volume and cooled. The crystalline acids were filtered off and treated with ten times their weight of boiling water as before. After filtration of the mixture, the filtrate deposited further crystals of crude allomucic-acid. This process was repeated with the original mother liquor until only a small amount of dark colored sirup remained. The several fractions of crude allomucic acid were washed with a little 95% alcohol and recrystallized to constant melting point. The total yield was **33** g. which melted at 167–168° with effervescence. The melting point as determined by Fischer[1] was 166–171°. The higher melting point of 172–173° reported by Patterson and Fulton[7] was found on rapid heating.

Allomucic **Mono-amide.**—Twenty grams of allomucic acid was dissolved in 300 cc. of water and boiled for forty minutes. The solution was allowed to stand overnight and was then filtered from a small amount of allomucic acid. The filtrate was evaporated under reduced pressure until most of the acid had crystallized out. After filtering, the solution was again evaporated until about **25 g.** of a sirupy mixture of acid and lactone was obtained. This was cooled in ice and treated with **30** cc. of concentrated ammonia water. After standing for about five hours, the solution was carefully neutralized with cold, concentrated hydrochloric acid, using Congo Red as indicator. On standing overnight a mixture of crystals of ammonium chloride and allomucic mono-amide was obtained. The former was removed by washing with water. The yield of practically pure amide melting at 175–175.5° was **2** g. Two additional crystallizations from water raised the melting point only **0.5'.** An additional gram of amide was obtained on concentrating the mother liquor.

Anal. **Calcd.** for $C_6H_{11}O_7N$: N, **6.69; 4.78 cc.** of **0.1** *N* NaOH, Found: N, **6.66; 0.1000 g.** required **4.77** cc. of **0.1** *N* NaOH.

Diethyl Allomucate.—This ester was prepared according to the method employed by Malaguti[4] in preparing diethylmucate. The yield was **42%.** It was also prepared as follows: **3.4** g. of allomucic acid was placed in a flask with **20** cc. of 1% hydrochloric acid in absolute ethyl alcohol. After refluxing for twenty minutes, a clear solution was obtained. Boiling was continued for three and one-half hours. The volume then was reduced about one-third by evaporation and the solution allowed to stand in the ice box overnight. The crystals of diethyl allomucate were filtered off and washed with absolute alcohol. The yield of crude product was **3.3** g. On recrystallization from alcohol 2.5 g. (58% of the theoretical) of pure ester was obtained, melting point **137–138°.** On evaporation of the mother liquor and washing, an additional **0.6** g. of crude material melting at about **130°** was obtained. The melting point of the second crop did not change after one recrystallization from alcohol.

Anal. Subs., **0.1000:** CO_2, **0.1653;** H_2O, **0.0624.** Calcd. for $C_{10}H_{18}O_8$: **C, 45.11;** H, **6.76.** Found: C, **45.08;** H, **6.93.**

Allomucic **Diamide.**—0.47 g. of diethyl allomueate was treated at room tempera-

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[7] Patterson and Fulton, J. *Chem. Soc.*, **50 (1927).**

ture with 3 cc. of concd. ammonia water. The ester dissolved and the diamide separated out almost immediately. It was washed thoroughly with water and alcohol and dried. The yield was 0.27 g., 75% of the theoretical. The substance is practically insoluble in water, ethyl alcohol and ether. It commenced to discolor at 185° and gradually darkened as the temperature was raised. It melted at 209°, with effervescence.

Anal. Calcd. for $C_6H_{12}O_6N_2$: N, 13.46. Found: N, 13.50, 13.38 (Kjeldahl).

Summary

1. An improved method for the preparation of allomucic acid is described.
2. Methods for the preparation of several new derivatives of the acid are presented.
3. A comparison is made of some of the properties of allomucic and mannosaccharic acids.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHT OF EDESTIN

BY THE SVEDBERG AND ALFRED J. STAMM[1]

RECEIVED MARCH 6, 1929 PUBLISHED JULY 5, 1929

The proteins that have thus far been subjected to the ultracentrifuge analysis in this Laboratory in order to determine their molecular weights as well as other physical characteristics have been water soluble[2] with the exception of serum globulin.[2f] This protein required only relatively small salt concentrations to hold it in solution. There are a number of other proteins of the globulin class that are soluble only in strong salt solutions. It was thus the authors' desire to see if the previously developed methods of study were completely applicable to the study of proteins dissolved in strong salt solutions.

The protein edestin, belonging to the vegetable globulin class, was chosen for this work so as to add another type of protein to the list of those studied. Edestin seemed especially suitable because of the ease with which it can be isolated and because of its definite crystalline structure, which is a strong indication of its homogeneity.

Preparation of Material.—Coarsely ground hemp seed (600 g.) was directly subjected to digestion and extraction with a mixture of 2000 cc. of 10% sodium chloride solution and 400 cc. of 2.1% disodium phos-

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[1] Fellow of the International Education Board.

[2] (a) T. Svedberg and R. Fåhraeus, THIS JOURNAL, 48, 430 (1926); (b) T. Svedberg and J B Nichols, *ibid.*, 48, 3081 (1926); (c) T. Svedberg and J. B. Nichols, *ibid.*, 49,2920 (1927); (d) T. Svedberg and N. B. Lewis, *ibid*, 50,525 (1928); (e) T. Svedberg and E. Chirnoaga, *ibid*, 50, 1399 (1928); (f) T. Svedberg and B. Sjögren, *ibid.*, 50, 3318 (1928).

phate.[3] After standing for twelve hours at room temperature the material was heated for two hours at 40° and then filtered through a filter cloth. The filtrate was clarified in a bucket centrifuge. Three volumes of water were added to each volume of the filtrate, causing precipitation of the extracted edestin. This was allowed to stand overnight in an ice box. The supernatant liquid was removed from the precipitate in the bucket centrifuge. After washing the precipitate several times by decantation with a dilute sodium chloride solution, the precipitate was dissolved in 10% sodium chloride. The reprecipitation and solution was repeated three times. The stock edestin was kept in an ice box in a precipitated form under dilute sodium chloride. A few drops of toluene were added to the solutions in the course of the preparation and to the stock precipitate and stock solutions to prevent bacterial action.

Due to the decreased solubility of edestin at low temperatures, as well as the decreased solubility of the phosphate buffers used, the stock solutions made up from the above precipitated edestin were dialyzed and kept at room temperature (about 18°). The course of the experiments showed that this had no deleterious effect.

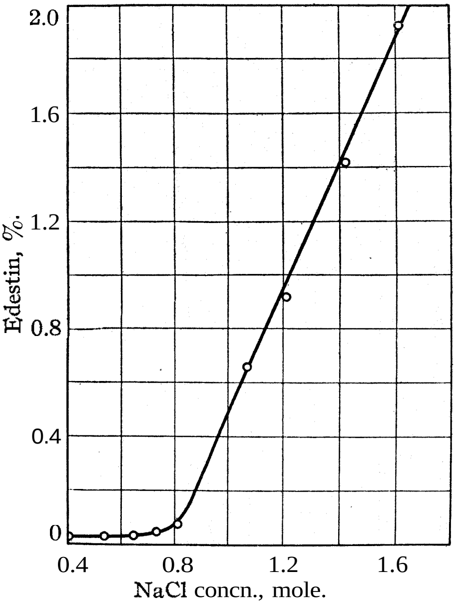

Fig. 1.

Solubility and Isoelectric Point.—Though edestin has perhaps been studied more than any other protein of this class, practically none of its physical characteristics are known with any degree of accuracy. Two different values have been obtained for the isoelectric point. Rona and Michaelis[4] found it to be at a PH 6.9 in phosphate buffers, and Michaelis and Mendelssohn[5] found it to be at PH 5.6 in acetate buffers. Because of this discrepancy, it seemed advisable to determine the isoelectric point from solubility measurements under the conditions used in this research, and at the same time to get the solubility information that would be of value in connection with the ultracentrifuge analysis.

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[3] The grinding of the hemp seed was kindly done for us in an experimental mill at the laboratory of Upsala Ångkvarn.

[4] Rona and Michaelis, Biochem. *Z.*, 28, 193 (1910).

[5] Michaelis and Mendelssohn, *ibid.*, 65, 1 (1914).

Three sets of solubility measurements were made. In each case the concentrations were determined by evaporating 2 cc. of the solvent and 2 cc. of the solution, and drying to constant weight in an oven at 105°. The solutions were allowed to stand in contact with an excess of edestin for several hours at room temperature (about 18°) and they were then clarified in a bucket centrifuge before pipetting off the samples for analysis. Figure 1 gives the solubility of edestin in different concentrations of sodium chloride solution. The solubility is small up to 0.8 M sodium chloride, but above this concentration the solubility increases rapidly. Figure 2 gives the changes in solubility of edestin in phosphate buffer solutions with the change in PH of the solvent. Curve A is for the phosphate buffer alone and Curve B for the phosphate buffer together with sodium chloride. Curve A gives a minimum solubility isoelectric point at PH 5.5 and B gives it at PH 5.4. A solution of edestin, in a previously boiled sodium chloride solution (PH 5.8), after twelve days' dialysis against the solvent, gave a PH of 5.5. As the sodium chloride has practically a negligible buffering action, the PH of the solution should be practically at the isoelectric point. These three values are in very good agreement and also check the value of the isoelectric point given by Michaelis and Mendelssohn.

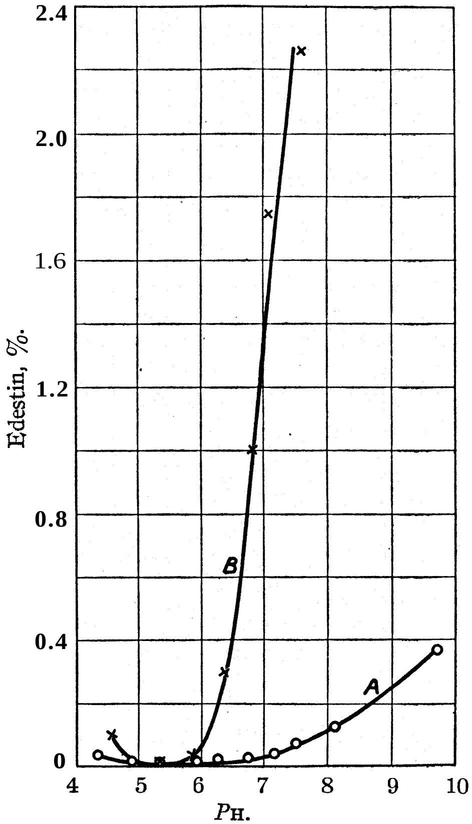

Fig. 2.—A, in phosphate buffer, total concn. 0.15 M; B, in phosphate buffer, total concn., 0.15 M + 0.735 M NaCl.

The solubility curves show that the solubility of edestin in buffered solutions is very small near the isoelectric point. The measurements to follow, that were made at the isoelectric point, have hence been made on unbuffered sodium chloride solutions. Measurements on solutions containing no sodium chloride could only be made at the higher PH values.

Specific Volume.—The partial specific volume of the protein was determined pycnometrically at 19.8°. Measurements were made on three different solutions of edestin of different *Ph* value and different concentration, as shown in Table I. Each of the solutions was dialyzed against

0.56

TABLE I

PARTIAL SPECIFIC VOLUME OF EDESTIN IN DIFFERENT SOLVENTS AT 19.8°

Edestin concn., %		**1.19**	*0.58*
Solvent	1.24 M NaCl	0.735 M NaCl *0.15* M Na_2HPO_4 *0.06* M KH_2PO_4	0.62 M NaCl *0.0375* M Na_2HPO_4 *0.026* M NaOH
Ph of soln.	*5.5*	*6.7*	**11.3**
Part. sp. vol.	*0.744*	*0.743*	*0.745*

the solvent for twelve days at room temperature (16 to 18°). The outer liquid was changed twice a day. The dialysis was conducted under a bell jar to minimize evaporation from the solvent. The table shows that the partial specific volume is not affected by the *Ph* of the solution over the range tested. These values agree, within the range of experimental error, with the partial specific volume of egg albumin, hemoglobin, serum albumin, serum globulin, phycocyan and phycoerythrin, as determined in this Laboratory.

Light Absorption.—The light absorption of cdestin solutions was determined with the Judd–Lewis spectrophotometer. The specific extinction coefficient, $\epsilon/c = 1/cd \log I_0/I$ (where c is the concentration in per cent., d the thickness of the solution, I_0 the intensity of the light beam after passing through the solvent and I the intensity of light after passing through the same thickness of solution), is plotted against the wave length of the light (see Fig. 3). Measurements were made upon 0.110 and 0.055% solutions of edestin in 1.24 M NaCl, *Ph* 5.5; 0.198, 0.099 and 0.0495% solutions of edestin 0.735 **M** in NaCl, 0.15 M in Na_2HPO_4 and 0.06 M in KH_2PO_4, *Ph* 6.7; a 0.090% solution of edestin 0.15 M in Na_2HPO_4, 0.0036 M in KH_2PO_4 and 0.0052 M in NaOH, *Ph* 9.7; a fresh 0.053% solution of edestin 0.62 M in NaCl, 0.0375 M in Na_2HPO_4 and 0.025 M in NaOH, *Ph* 11.3; a similar solution to the latter made up from a solution five days old containing originally 0.58% of edestin; and a 0.089% solution of edestin 0.206 M in NaCl and 0.0167 M in HCl, *Ph* 1.S. All of these solutions gave practically

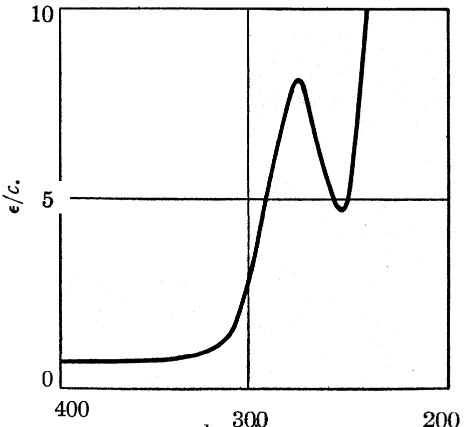

Fig. 3.

identical curves so only the average value is plotted. The absorption showed a maximum at 276$\mu\mu$, and a minimum at 254$\mu\mu$.

Determination of the Molecular Weight

Sedimentation Velocity Method.—The apparatus and the method have been so completely described in previous publications[2c,d,e,f,6] that no attempt will be made to repeat the description here. The modifications described by Svedberg and Sjögren[2f] were effective in this work. As the maximum light absorption of edestin is similar to that for the other proteins studied, the same optical system and the same chlorine and bromine filters were used.

The molecular weight is given by the relation

$$M = \frac{RTs}{D(1 - V\rho)}$$

where R is the gas constant, T the absolute temperature, *s* the specific sedimentation velocity or $1/\omega^2x\cdot dx/dt$, D the diffusion constant, V the partial specific volume of the protein, p the density of the solvent, *x* the distance from the axis of rotation, w the angular velocity and *t* the time.

Table II gives the results of a typical run made with an edestin solution at the isoelectric point. The constancy of the values for the specific

TABLE II

RESULTS OF A TYPICAL SEDIMENTATION VELOCITY RUN MADE UPON AN ISOELECTRIC SOLUTION OF EDESTIN IN 1.24 M SODIUM CHLORIDE SOLUTION

Concentration, 0.56%; PH of solution, 5.5; V = 0.744; ρ = 1.0479; rel. vis. of solvent, 1.0690; length of column of solution, 1.38 cm.; thickness of column, 0.60 cm.; average speed, 23,900 r.p.m.; aperture of objective, F:36; time of exposure, 80 sec.; time interval between exposures, 35 min.; temperature, 21.0°.

Sedimentation				Diffusion		
AX, cm.	Mean X, cm.	Centrif. force, ω^2X X 10^{-7}	s_{20} cm./sec. per cm./sec.^{2} X 10^{13}	Time, sec.	Mean Z, cm.	D_{20} cm./sec. X 10^7
0.066	4.653	2.93	10.48	2,520	0.033	4.61
.067	4.719	2.98	10.43	4,620	.045	4.67
.067	4.786	3.05	10.19	6,720	.052	4.29
.065	4.853	3.09	9.75	8,820	.065	5.11
.065	4.917	3.09	9.75	10,920	.073	5.20
.070	4.985	3.07	10.57	13,020	.079	5.11
.070	5.055	3.06	10.60	15,120	.086	5.22
.067	5.123	3.16	9.85	17,220	.098	5.95
		Av.	10.2 X 10^{-13}			5.02 X 10^{-7}

Av. molecular weight, 225,000.

"Mean Z" is the mean of the distances on the photometer curves from the point where the concentration is 50% to the points where the concentrations are 25 and 75%, respectively, the concentration in the unchanged part of the solution being taken as 100%.[2c]

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[6] The Svedberg, "Colloid Chemistry," 2nd ed., Chemical Catalog Co., Inc., New York, 1928.

sedimentation velocity s and the diffusion constant D indicates that the cdestin is mono-disperse and that the solvent shows no time function effect upon the systems. The edestin further settled so as to give clear buffer at the top of the cell, thus showing that there was no non-centrifugible material present with a light absorption between 250 and $290\mu\mu$, the wave lengths of the light entering the cell.

Figure 4 gives the concentration curves from which the data of Table II were obtained. The curves have been corrected for the sector shape of the cell and the variation of the centrifugal force with distance from the center of rotation. The dotted curves for each represent the theoretical diffusion curves of a substance of only one molecular species when subjected to the same experimental conditions. The deviations obtained are well within the range of experimental error.

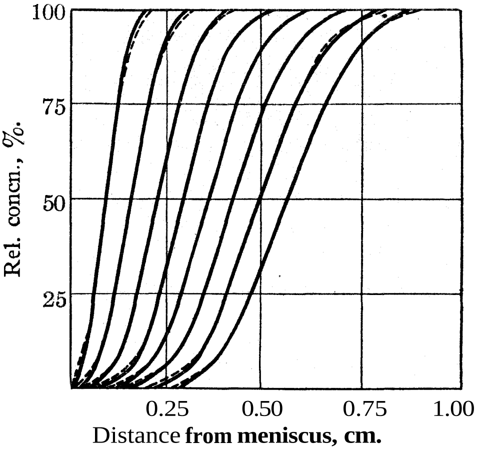

Fig. 4.

Table III gives a summary of all of the sedimentation velocity runs. The effect of varying only the edestin concentration was determined for two different solvents. The specific sedimentation velocities and the diffusion constants show no regular shift between the concentrations of 1.16 and 0.193% in 1.24 M NaCl, P_H 5.5. The resulting molecular weight values are constant within experimental error over this range. The same is true in the solutions at P_H 6.7 from a concentration of 1.38% edestin to a concentration of 0.155%. At the concentration of 0.108 there is an appreciable change in the specific sedimentation velocity and diffusion constant, indicating a change in the molecular dispersion of the edestin. Dissociation has very likely taken place in this dilute solution. The abnormal specific sedimentation velocity and the continuous shift in the apparent diffusion constant from 3.1 at the start of the run to 11.3 at the end of the run indicate the heterogeneity of the system. The molecules of different molecular weight settling at different speeds caused a spreading or blurring at the sedimentation boundary, which according to the methods of calculation is included with the true diffusion. Though such runs as this cannot be quantitatively analyzed and the true molecular weights calculated, they show very nicely in a qualitative way what has happened to the solution.

The molecular weights calculated from the data of all of the runs at

TABLE III

SUMMARY OF RESULTS BY THE SEDIMENTATION VELOCITY METHOD

No.	Solvent, M NaCl	Solvent, M Na_2HPO_4	Solvent, M KH_2PO_4	PH soln.	Density of soln.	Rel. vis. of soln.	Concn. of edestin, %
1	1.24	..	..	5.5	1.0479	1.069	1.16
2	1.24	..	..	5.5	1.0479	1.069	0.560
3	1.24	..	..	5.5	1.0479	1.069	.290
4	1.24	..	..	5.5	1.0479	1.069	.193
5	0.735	0.15	0.06	6.7	1.0529	1.120	1.38
6	.735	.15	.06	6.7	1.0529	1.120	0.890
7	.735	.15	.06	6.7	1.0529	1.120	.445
8	.735	.15	.06	6.7	1.0529	1.120	.222
9	.735	.15	.06	6.7	1.0529	1.120	.155
10	.735	.15	.06	6.7	1.0529	1.120	.108
11	Like 5–10 with 55.7% of water added			6.7	1.0225	1.055	.296
12	..	.0715	.0017	7.9	1.0073	1.031	.150
13	.0052[a]	.15	.0036	9.7	1.0171	1.075	.300
14[b]	.62	.075	.0018	9.7	1.0325	1.072	.580
15	.62	.0375	.025[a]	11.3	1.0295	1.035	.580
16	.62	.0375	.025[a]	11.3	1.0295	1.035	.580
17	.206	.00217[c]	..	3.1	1.0079	1.011	.193
18	.206	.0167[c]	..	1.8	1.0079	1.011	.193

[a] Sodium hydroxide. [b] Sodium hydroxide, 0.0026 M, added. [c] Hydrochloric acid.

No.	Av. r.p m. of centr.	Non-centrif. material, %	s_{20} cm./sec. per cm./sec^2 $\times 10^{13}$	Dm cm.^{2}/sec. $\times 10^7$	Water basis s_{20} $\times 10^{13}$	Water basis D_{20} $\times 10^7$	Mol. wt.
1	23,900	1	10.8	5.63	13.4	6.02	213,000
2	23,900	0	10.2	5.02	12.7	5.37	225,000
3	23,800	0	10.4	5.49	12.9	5.88	209,000
4	24,600	2	10.0	5.00	12.4	5.35	221,000
5	23,500	7	9.46	4.83	12.5	5.40	219,000
6	43,800	..	9.45	..	12.5	..	.....
7	23,700	7	9.54	5.11	12.6	5.72	209,000
8	23,600	9	9.70	4.98	12.8	5.58	218,000
9	24,300	11	9.32	4.99	12.6	5.59	209,000
10	23,800	14	[8.70]	[7.48]	..	..	.....
				Av.	12.77	Av. 5.62	Av. 215,000
11	23,400	7	11.8	5.63	13.3	5.94	213,000
12	24,600	..	12.5	5.67	13.1	5.85	214,000
13	23,700	4	12.1	5.93	13.7	6.37	204,000
14	23,800	0	10.75	5.44	12.7	5.83	208,000
15	23,700	16	4.82	5.7[a]	5.47	5.90	.....
16	42,500	6	4.90	6.1[a]	5.55	6.32	.....
17	23,700	28	12.2	..	12.7	..	.....
18	24,500	50	9.16	..	9.48	..	.....

[a] Extrapolated values (see Fig. 5).

PH 5.5 and PH 6.7, with the exception of the one above cited where dissociation took place, are in very good agreement. The average molecular weight of 215,000 is almost exactly the same as that of phycoerythrin obtained by Svedberg and Lewis. This molecular weight is considerably larger than any of the estimates that have been made from analytical data; Cohn[7] gives 29,000 as the minimal molecular weight of edestin. Osborne[8] gives 7250 as the minimal molecular weight from the acid combining capacity and chemical composition. Estimates by the osmotic pressure methods cannot be made as in the case of several of the other proteins, because high electrolyte concentrations are necessary to hold the edestin in solution and they would exert a far greater pressure than the edestin itself.

In order to compare the specific sedimentation velocity and the diffusion constant in the different solvents, the experimentally determined values have been converted to a basis of sedimentation and diffusion in pure water. The specific sedimentation velocity depends inversely upon the viscosity of the solvent and directly upon the difference in density between the particle and the solvent. The experimental values have thus been multiplied by the relative viscosity of the solvent and the ratio between the density differences in water and in the solvent. As the diffusion depends inversely upon the viscosity, it has been multiplied by the relative viscosity. The values of s on the water basis for the solutions at P_H 5.5 and 6.7 show a maximum deviation of 5%, and a mean deviation of 2% from the average value. The values of D show a maximum deviation of 7% and a mean deviation of 4% from the average.

The percentage of non-centrifugible normal light-absorbing material from each run is also included in Table III. These values were obtained from the deviation of the light absorption of the liquid at the top of the cell from that of the pure buffer. For all of the solutions at P_H 5.5 it was very small. In the case of the solution of P_H 6.7 it was somewhat larger and showed a slight increase with a decreased edestin concentration, as has been noted with other proteins.[2f] The fact that the solutions at P_H 6.7 were considerably older at the time the runs were made than those at P_H 5.5 may account for the slight decomposition of the former. In none of these cases, however, is the percentage of non-centrifugible material present sufficient to interfere with the determinations.

The effect of the dilution of the solvent with water is shown by Run 11, Table III. The values of the specific sedimentation velocity, diffusion constant and molecular weight are quite normal. The fact that the concentration of the solvent and its saline composition can be varied over a considerable range without affecting the results indicates the applicability of the sedimentation velocity method to the study of the molecular weights of proteins in strong salt solutions.

[7] Cohn, *Physiol. Rev.*, 5, 360 (1925).

[8] Osborne, THIS JOURNAL, 24, 39 (1902).

Table III also shows the effect of varying the *PH* of the solution. The results show that edestin is stable over a considerable range of Pa on the alkaline side of the isoelectric point. Run 13 shows the results for a sample that was made up three months before the measurements were made. Not only is the molecular weight normal, but the sedimentation curves further show that only 4% of non-centrifugible material of normal light absorption can be present. This is even less than the amount present in the case of several of the runs at *PH* 6.7.

A further increase in the *PH* above *PH* 9.7 shows a definite decomposition or dissociation. Runs 15 and 16 were at a *PH* of 11.3. The former was run at a speed of 23,900 r.p.m. and the latter at 42,500 r.p.m. The specific sedimentation velocities are in good agreement but they are less than half of the normal value. The diffusion constants, which are apparent rather than real because of the heterogeneity of the system, are plotted in Fig. 5 for the different times of sedimentation. In the case of the high-speed run the change of the apparent diffusion with time is greater than for the low-speed run, because of the greater separation of the sedimentation boundaries of the different molecular species present. It is of interest to note that the ratio of the slopes of the two curves after a considerable time of centrifuging approaches the square of the ratio of the centrifugal forces, that is, the *Z* displacements per unit of time approach proportionality to the centrifugal forces applied. This means that with increased time the proportion of the apparent diffusion constant that is caused by true diffusion becomes less and less, and that the spreading of the sedimentation boundaries predominates. When the apparent diffusion curves are extrapolated to zero time the converse should be true for the resulting values. There should be no spreading of the boundaries and the diffusion values should be real, and a sort of average value for the diffusion constants of the various constituents present in the mixture. It will be shown later that this is the case.

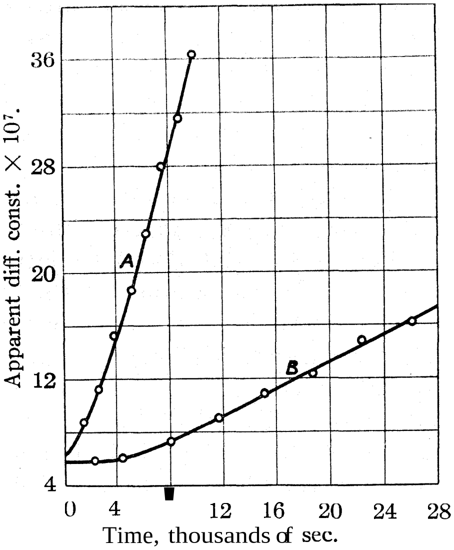

Fig. 5.—A, 42,500 r.p.m.; B, 23,900 r.p.m.

A further analysis of the data of Run 15 is given in Fig. 6. The experimental sedimentation curve E corrected for the sector shape of the cell and the variation of the centrifugal force with distance from the center of rotation is given for the longest time of centrifuging (corresponding to the highest point on Curve A (Fig. 5). The dotted curves A, B and C are the theoretical sedimentation curves for normal edestin, a protein of one-half the normal molecular weight and one of one-third the normal molecular weight, respectively, each of which is subjected to the actual experimental conditions. The specific sedimentation velocities and diffusion constants used for the fractional molecular weight calculations were the actual experimental values obtained for the proteins that have these molecular weights.[2c,d,f] The dotted curve, D, is for the theoretical mixture of 15% A, 30% B and 55% C, respectively. This curve

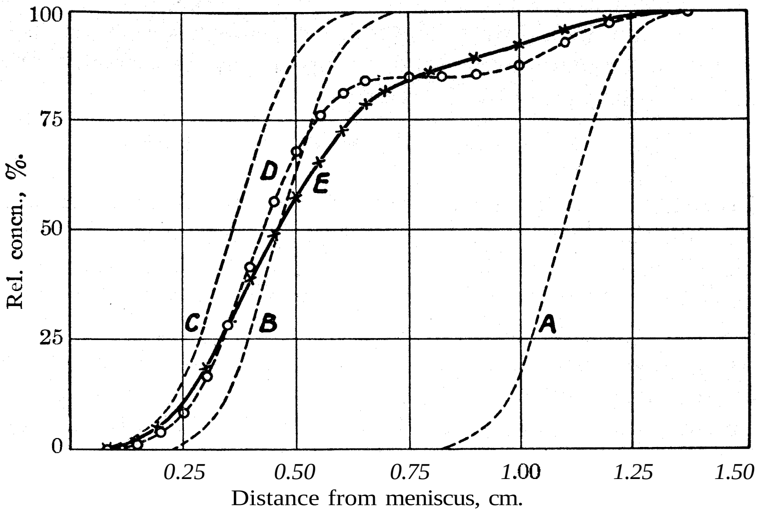

Fig. 6.—*A*, Theoretical curve for normal edestin; B, for *a* protein of $M = 106{,}000$; C, $M = 68{,}000$; *D*, *15%* A, *30%* B, and 55% C; E, actual experimental curve for edestin at $P_H = 11.3$.

shows a fair agreement with the actual experimental curve, E. It is especially good at the ends, the deviation being almost entirely near the inflection point. Similar curves for shorter times of sedimentation showed far better agreement between the observed and the theoretical curves. Such an analysis as this of course cannot prove the molecular constitution of the mixture, for perhaps other combinations will satisfy the experimental conditions as well as this. It serves, however, to show the general nature of the mixture. In the last section of this paper the constitution of this mixture will be shown quite definitely to be that represented here.

Edestin is far less stable on the acid side of the isoelectric point than on the alkaline side. Decomposition takes place both at P_H 3.1 and 1.8. Though the specific sedimentation velocity is almost normal, showing the presence of normal edestin, the diffusion constant is definitely of the apparent diffusion type pictured above. The decomposition, however, is quite different from that on the alkaline side of the isoelectric point, as the decomposition is mostly into material of such a low molecular weight that no sedimentation will take place. This can be seen readily by comparing the percentages of non-centrifugible material present for each of the runs listed in Table III. Slight irregularities in the sedimentation curves for both of these acid runs indicate that there are some centrifugible decomposition products present, as is required by the abnormal diffusion constant. Though these cannot be identified definitely, it seems probable from the curves that a material of one-half of the normal molecular weight is present.

Sedimentation Equilibrium Method.—A few runs were made by the sedimentation equilibrium method as previously described.[2a,b,d,e] The molecular weight is given by the relation

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)}$$

c_1 and c_2 are the concentrations at the distances x_1 and x_2 from the center of rotation and the other symbols have the same significance as previously.

Table IV gives the results of a typical run showing that there is no regular change of molecular weight with height. Table V gives a summary of all of the equilibrium runs. The molecular weights obtained by this method agree quite well with the values obtained by the sedimentation velocity method. An unsuccessful attempt was made to determine the molecular weight of the protein at PH 11.3 by this method.

TABLE IV

RESULTS OF A TYPICAL SEDIMENTATION EQUILIBRIUM RUN MADE UPON AN ISOELECTRIC SOLUTION OF EDESTIN IN 1 24 M SODIUM CHLORIDE SOLUTION

Concentration, 0.58%; PH of solution, 5.5; $V = 0.744$; $\rho = 1.0479$; length of column of solution, 0.59 cm.; thickness of column, 0.2 cm.; distance of outer end of solution from axis of rotation, 5.95 cm.; average speed, 5280 r.p.m.; aperture of lens, F:25; time of exposures 1, 2 and 3 min.; exposures made after 30, 35 and 45 hours of centrifuging.

Distances, cm.		Mean concn. (orig. soln. = 1.00)		No of exposures	Mol. wt.
x_2	21	c_2	c_1		
5.86	5.81	2.09	1.76	6	222,000
5.81	5.76	1.76	1.48	9	223,000
5.76	5.71	1.48	1.29	12	179,000
5.71	5.66	1.29	1.12	12	185,000
5.66	5.61	1.12	0.95	12	216,000
5.61	5.56	0.95	.81	12	212,000
5.56	5.51	.81	.68	12	238,000
5.51	5.46	.68	.58	9	217,000
5.46	5.41	.58	.49	9	234,000
5.41	5.36	.49	.42	9	214,000
				Mean	214,000

The results showed definitely that the edestin had decomposed or dissociated into several molecular species of the order of molecular weight of those predicted by the sedimentation velocity method, but no quantitative results could be obtained because of the complexity of the system and the long time required to obtain equilibrium during which further changes in the protein may have resulted.

TABLE V

SUMMARY OF THE RESULTS BY THE SEDIMENTATION EQUILIBRIUM METHOD

No.	1	2	3	
Solvent, NaCl	1.24 M	0.735 *M*	0.735 M	
Solvent, Na_2HPO_4	...	.15 M	.15 M	
Solvent, KH_2PO_4	...	.06 M	.06 M	
PH of solution	5.5	6.7	6.7	
Concn. of edestin, %	0.580	0.595	0.595	
Mean speed, r.p.m.	5280	4970	4900	
Exposures after hours	30, 35, 45	29, 38	30, 36, 44	
Molecular weight	214,000	209,000	202,000	Mean, 208,000

Sedimentation Velocity Method as Modified by **Lamm.**—Ole Lamm, working in this Laboratory, has developed a new method for determining the changes in concentration in a sedimenting system based on the measurement of the changes in the refractive index of the system. The theory of the method has been described by Lamm.[9] For a complete description of the method the reader is refered to the above publication and subsequent publications of Lamm to follow. It suffices to state here that the measurements yield directly a function which is proportional to the change in the concentration with changes in height, that is, a first derivative curve. As the results will show, such a function gives the abnormalities due to the presence of several molecular species in the system much more definitely than the simple concentration–height relationship obtained by the old method. A run made by the new method on a 0.487% solution of edestin in 1.24 M sodium chloride (average speed, 24,300 r.p.m.) gave a molecular weight of 222,000, a specific sedimentation velocity of 12.4×10^{-13} and a diffusion constant of 5.30×10^{-7} on a water basis. These values all agree well with the values given in Table III.

In Fig. 7 is plotted the function of the change in concentration with height against the height for a 0.487% solution of edestin at *PH* 11.3 after one and one-half hours' sedimentation. Instead of obtaining the simple one-maximum curve that would result if only one molecular species were present, there are three definite maxima. The three dotted curves

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[9] Lamm, *Z. physik. Chem.*, 138,313 (1928). The application of the method to the ultracentrifuge was not as yet published at the time of the preparation of this manuscript, but should appear in print soon. The authors are grateful to Lamm for granting them permission to publish their results obtained by the new method before his complete description of the method has appeared in print.

represent the three simple curves whose summation is the experimental curve. From the position and the shape of these three curves the specific sedimentation velocities and the diffusion constants of each of the constituents can be calculated according to the method which Lamm will describe. Table VI gives a summary of the results of this run, obtained from the curves of Fig. 7, as well as from similar curves for different times of centrifuging. Because of the high centrifugal force used the normal edestin is so completely removed from the system in two hours that only two values for the specific sedimentation velocity could be obtained from the data. The small percentage of the normal edestin present, as is shown by the relatively low maxima, made it practically impossible to obtain diffusion data for this constituent. The specific sedimentation velocity for Constituent 1, however, shows definitely that it represents the original normal edestin. Both the specific sedimentation velocities and the diffusion constants for Constituent 2 are very close to the values for serum, globulin and phycocyan,[2d,f] and those for Constituent 3 are very close to the values for hemoglobin and serum albumin.[2e,f] The data thus definitely show that edestin at a PH of 11.3 dissociates into particles having one-half and one-third of the original molecular weight, and that these dissociation products have the same specific sedimentation velocity and diffusion constant as the other proteins that have the same molecular weights. This run by the new method further shows that the proportions of the three constituents present are of the same order of magnitude as in the theoretical calculation of Fig. 6.

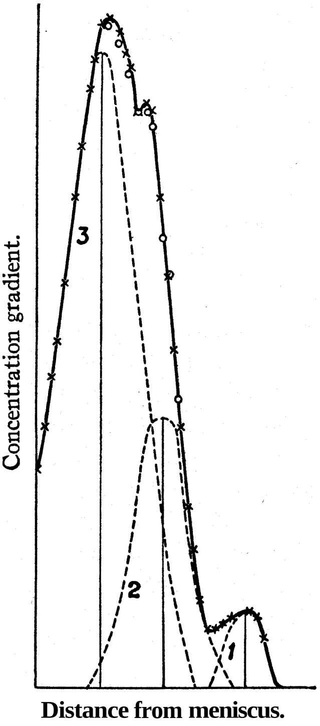

Fig. 7.

This one illustration shows very nicely the possibilities of applying the new method to the study of mixed proteins. Further work along this line is now under way at this Laboratory and should yield more important data regarding the dissociation of proteins.

Discussion of Results

This research has shown quite definitely the applicability without modifications of both the sedimentation velocity and sedimentation equilibrium methods to the study of proteins dissolved in strong salt solutions.

TABLE VI

SUMMARY OF THE RESULTS OBTAINED ON EDESTIN AT P_H 11.3 BY THE NEW METHOD DEVELOPED BY OLE LAMM

Edestin concentration, 0.487%; solvent 0.62 M in NaCl; 0.0375 *M* in Na_2HPO_4; 0.025 M in NaOH; P_H of solution, 11.3; density of solvent, 1.0295; relative viscosity of solvent, 1.0350; thickness of column of solution, 0.60 cm.; average speed, 42,500 r.p.m.; average temperature, 21.2°

	Specific sedimentation velocities at 20°		
Time, hours	Constituent 1	Constituent 2	Constituent 3
1–1.5	10.44×10^{-13}	5.73×10^{-13}	3.29×10^{-13}
1.5–2	10.59×10^{-13}	5.22×10^{-13}	3.40×10^{-13}
2–2.5	....	4.78×10^{-13}	3.16×10^{-13}
2.5–3	....	5.28×10^{-13}	3.76×10^{-13}
3–3.5	....	5.23×10^{-13}	3.77×10^{-13}
Av.	10.52×10^{-13}	5.25×10^{-13}	3.47×10^{-13}
Water basis values	11.9×10^{-13}	5.94×10^{-13}	3.94×10^{-13}

		Diffusion constants at 20°	
Time, sec.	Constituent 1	Constituent 2	Constituent 3
4,020	....	4.78×10^{-7}	5.43×10^{-7}
5,820	....	4.68×10^{-7}	6.02×10^{-7}
7,620	....	5.25×10^{-7}	5.75×10^{-7}
9,420	....	5.91×10^{-7}	5.35×10^{-7}
11,220	....	....	6.52×10^{-7}
13,020	....	....	5.98×10^{-7}
	Av.	5.15×10^{-7}	5.84×10^{-7}
Water basis values	....	5.33×10^{-7}	6.05×10^{-7}
Molecular weight	....	106,000	62,200

The specific sedimentation velocity values obtained in different solvents can be converted to a basis of sedimentation in water merely by multiplying by the relative viscosity of the solvent and the ratio of the difference in densities between the particle and the solvent, in water and in the solvent under consideration. The diffusion constant values can be converted to a basis of diffusion in pure water by merely multiplying by the relative viscosity of the solvent. The results in Table III show very nicely the constancy of both the specific sedimentation velocity and diffusion constant when corrected to a water basis for all of the solvents except those in which dissociation took place.

The molecular weight of normal edestin is practically the same as that of phycoerythrin. The specific sedimentation velocity and diffusion constant are likewise the same within experimental error. Calculation of the radius of the particle by applying both Stoke's law and Einstein's law shows that the edestin molecules are practically spherical as in the case with phycoerythrin.[2d]

This research gives considerable further evidence in favor of the senior author's theory that the proteins all have molecular weights that are integral multiples of the molecular weight of egg albumin, namely, 34,500.

Normal edestin has a molecular weight very close to six times this value. Every one of the proteins thus far studied in this Laboratory has a molecular weight of either 1, 2, 3 or 6 times that of the egg albumin with the exception of the two hemocyanins, which are such large multiples that it is impossible to determine whether they are integral multiples.

The nature of the dissociation products of edestin at P_H 11.3, obtained by the new method of Lamm, gives perhaps the best single piece of evidence obtained to date of the validity of the theory. Not only are the molecular weights of the dissociation products even multiples, but they are the same multiples as other known proteins and have the same specific sedimentation velocities and diffusion constants. No protein with a molecular weight 4 times that of egg albumin has ever been found. It is of interest to note that there was no evidence of any such multiple molecular weight dissociation product either, or a multiple of 1.5 as might be expected if the dissociation took place in two steps. A more extended research upon the dissociation products of edestin as well as of other proteins outside of their normal P_H stability range will undoubtedly settle this theoretical consideration definitely.

The expenses connected with these experiments have been defrayed by grants from the Nobel Fund of Chemistry and from the foundation "Therese och Johan Anderssons Minne."

Summary

1. The previously developed ultracentrifuge methods for determining the molecular weights of proteins have been shown to be completely applicable to the study of proteins dissolved in strong salt solutions.

2. The normal molecular weight of edestin was found to be 212,000 ± 10,000, the average specific sedimentation velocity 12.8×10^{-13} cm./sec. and the average diffusion constant 5.6×10^{-7} cm.^{2}/sec. both on a water basis at 20°.

3. The edestin concentration showed no effect upon the resulting molecular weight, above a concentration of 0.1%. Below this value definite dissociation or decomposition took place.

4. Edestin was shown to be quite stable and to give a normal molecular weight on the alkaline side of the isoelectric point (P_H 5.5 by solubility measurements) as high as a P_H of 9.7. At a P_H of 11.3 definite dissociation took place. Edestin was found to be quite unstable on the acid side of the isoelectric point, definite*dissociation taking place at P_H 3.1.

5. Employing a new method developed by Ole Lamm at this Laboratory for determining the concentration gradients in the sedimentation systems, the molecular constitution of dissociated edestin at a P_H of 11.3 was definitely determined. Under the conditions of the experiment given,

molecules of one-half and one-third of the normal molecular weight are present together with the normal.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE COLLEGE OF THE CITY OF NEW YORK]

THE FATTY ACIDS ASSOCIATED WITH RICE STARCH

BY LEO LEHRMAN

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It has been shown that in several naturally occurring starches fatty acids are combined with carbohydrate.[1] In the case of corn and rice the fatty acids constitute part of the molecule of one of the components, namely, the α-amylose.[2] The fatty acids liberated by the hydrolysis of corn starch free from extraneous material have been identified and their amounts determined.[1b,3] From a review of the "fat by hydrolysis,"[1b] acid number and iodine number of the fatty acids liberated from corn and rice starch free from extraneous material,[1b] a difference in amounts and possibly in kind is apparent. Therefore, it is important that these fatty acids which are in the rice starch molecule[1] (a-amylose portion) should be determined both qualitatively and quantitatively. This would enable a comparison of these two starches and furnish additional evidence in the understanding of the different behavior of the starches.

In the course of the investigation the probable absence of sterols or other substances that might occur in the starch and be present in the liberated fatty acids was shown. As the fatty acids occurring in the germ are present as glycerides, the aqueous filtrate from the hydrolysis was examined for glycerol; a negative result was obtained. This is added evidence that the fatty acids identified were not present extraneously in the starch.

Experimental Part

Mixed Fatty Acids from Rice Starch.—The rice starch[4] which was used as the starting material had a negligible amount of extractable extraneous material, using petroleum ether as the solvent. In the course of the work a total of twenty pounds was used. The hydrolysis[1b] was carried out using hydrochloric acid and a much more concentrated suspension of the rice starch. Five pounds of the starch yielded a suspension of 3.5 liters; the acid solution was made up by diluting 525 cc. of concentrated hydrochloric acid to 1.5 liters. The filtrate from the hydrolysis, which had a dark brown color, was reserved for the examination for glycerol. The fat by hydrolysis, obtained by

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[1] (a) Sostegni, *Gazz. chim. ital.*, 15, 376 (1885); (b) Taylor and Nelson, THIS JOURNAL, 42, 1726 (1920); (c) Aoi, *J. Chem. Soc., Japan*, 44, 755 (1923).

[2] Taylor and Iddles, Ind. *Eng. Chem.*, 18,713 (1926).

[3] Taylor and Lehrman, THIS JOURNAL, 48, 1739 (1926).

[4] The author wishes to thank Stein, Hall and Co., Inc., New York City, for their kindness in supplying this material.

extracting the dry residue with petroleum ether and then allowing the solvent to evaporate spontaneously, was a light yellow colored solid; five pounds of the original rice starch gave **14.75** g. of mixed fatty acids free from traces of the solvent.

Examination of Filtrate for Glycerol.—In order to concentrate the glycerol if it was present, a distillation of some of the filtrate from the hydrolysis was attempted but there was so much frothing that the process had to be stopped. Two liters was put in a large beaker and evaporated to about **300** cc., a dark brown precipitate being obtained. This was filtered off and the filtrate extracted with chloroform. After the chloroform was distilled off, a black tarry material was left. This was boiled up with a small amount of water, filtered, treated with potassium permanganate in acid solution and tested for formaldehyde.[5] The result was negative.

In order to be sure that the acid present from the hydrolysis had no effect in the subsequent procedure, one liter of the filtrate from the hydrolysis was neutralized with calcium carbonate, extracted with chloroform and the chloroform distilled off. The small amount of tarry material left gave negative results for glycerol.[5]

Isolation and Identification of Saturated Fatty Acid.—The mixed fatty acids were dissolved in alcohol, the solution chilled in an ice–salt mixture until nearly solid, filtered quickly by suction and washed with several portions of cold alcohol. The solid white residue was recrystallized several times from alcohol, when it gave a melting point of 62°.

The phenylhydrazide, made by heating with an excess of phenylhydrazine,[6] was a white crystalline solid, m. p. 110°,[7] which corresponded with that made similarly from pure palmitic acid.

The molecular weight of the acid was determined by dissolving a weighed amount in neutral alcohol and titrating with standard alkali to phenolphthalein, running a blank at the same time.

Anal. Subs., **0.0784, 0.1245: 7.50, 11.86** cc. of $N/25$ NaOH. Calcd. for palmitic acid, $C_{16}H_{32}O_2$: mol. wt. **256.3.** Mol. wt. found: (monobasic acid) **261.3, 262.4.**

Anal. Subs., **0.1252, 0.1163:** CO_2, **0.3446, 0.3206;** H_2O, **0.1387, 0.1295.** Calcd. for palmitic acid, $C_{16}H_{32}O_2$: C, **74.91;** H, **12.59.** Pound: C, **75.06, 75.18; H, 12.40, 12.46.**

From the above data the presence of palmitic acid in the mixed fatty acids is shown.

Identification of Unsaturated Fatty Acids

A. Oxidation.—The mixture of unsaturated fatty acids separated from the saturated fatty acid by means of the magnesium soap alcohol method[3] was a light brown oil.

A portion of this mixture of unsaturated fatty acids was oxidized with potassium permanganate in alkaline solution.[8] It was found that about half of the oil could bc recovered unoxidized, so the oxidation was repeated on this and the product combined with that from the first oxidation. After the hydroxy acids were filtered off, they were washed with water and allowed to dry on the filter paper. In the course of this investigation it was found that the lower hydroxy acid fraction (ether-soluble part) always contained a small amount of the higher hydroxy acid which was difficult to eliminate. This was due to the slight solubility of the higher hydroxy acid in ether, a fact not mentioned previously. In order to make a sharper separation a different solvent was sought and it was found that chloroform on prolonged extraction dissolves the lower hydroxy acid and none of the higher.

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[5] Gettler, *J. Biol. Chem.,* **42,311 (1920).**

[6] Brauns, THIS JOURNAL, **42, 1480 (1920).**

[7] J. van Alphen, *Rec. trav. chim.*, **44, 1064 (1925).**

[8] Lapworth and Mottram, J. *Chem. Soc., 127,* **1628 (1925).**

After several recrystallizations from chloroform and a final one from ether, a white crystalline solid was obtained, m. p. 124–126". Equal parts of this substance were mixed with dihydroxystearic acid, m. p. 127–128" (obtained from corn starch),[3] ground to a fine powder and the melting point determined (123–124").

Anal. Subs., 0.0619, 0.1072; CO_2, 0.1549, 0,2691; H_2O, 0.0608, 0.1074. Calcd. for dihydroxystearic acid, $C_{18}H_{36}O_4$: C, 68.29, H, 11.47. Found: C, 68.25, 68.44; H, 10.99, 11.21.

The silver salt was prepared9 and the molecular weight determined by igniting a weighed amount in a porcelain crucible and weighing the residue of metallic silver.

Anal. Subs., 0.0365: Ag, 0.0090. Calcd. for dihydroxystearic acid, $C_{18}H_{36}O_4$: mol. wt., 316.3. Found: 330.7.

The above results indicate the presence of oleic acid in the mixture of unsaturated fatty acids.

The residue of the chloroform extraction of the solid hydroxy acids was extracted with hot water and the solution allowed to cool slowly, silky white crystals coming out. These crystals were filtered off, recrystallized from water and dried, giving a melting point of 154–155°.

Anal. Subs., 0.1354, 0.1421: CO_2, 0.3084, 0.3245; H_2O, 0.1239, 0.1314. Calcd. for tetrahydroxystearic acid, $C_{18}H_{36}O_6$: C, 62.02; H, 10.42. Found: C, 62.12, 62.28; H, 10.24, 10.35.

These data indicate the presence of linolic acid in the mixture of unsaturated fatty acids.

The filtrate from the filtration of the insoluble hydroxy acids was now examined for higher hydroxy acids according to the method of Lewkowitsch[10] but the results were negative, thus indicating the absence of acids more unsaturated than linolic.

B. **Bromination.**—A sample of the unsaturated fatty acid mixture was brominated[11] and gave no ether-insoluble bromides, indicating the absence of acids more unsaturated than linolic, which substantiates the results as obtained by oxidation. After evaporation of the ether, the residue was recrystallized several times from petroleum ether, yielding white crystals, m. p. 113°.

Anal. (Carius). Subs., 0.1587, 0.1637; AgBr, 0.1984, 0.2050. Calcd. for tetrabromostearic acid, $C_{18}H_{32}O_2Br_4$: Br, 53.33. Found: Br, 53.18, 53.27.

These data are additional indication of the presence of linolic acid in the mixture of unsaturated fatty acids.

Examination for **Other** Substances,—The result of a sodium fusion on the mixed fatty acids showed the absence of nitrogen, sulfur and halogens. A fusion of another sample of the mixed fatty acids with a mixture of equal parts of sodium carbonate and sodium nitrate showed the absence of phosphorus.

During the alcoholic saponification of the mixed fatty acids necessary in the preparation of the magnesium soaps[3] no unsaponifiable matter was noticed. The Liebermann–Burchard[12] test for phytosterol was also

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[9] Clarke, "A Handbook of Organic Analysis," 2nd ed., p. 216.

[10] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th ed., Vol. I, p. 564.

[11] **Ref.** 10, p. 573.

[12] Ref. 10, p. 270.

negative. The modified Kerr and Sorber[13] method for detecting phytosterol was applied but again the results were negative.

Thus the results given above show the presence of three fatty acids, that is, palmitic, oleic and linolic, and the probable absence of other substances in the fatty acid mixture obtained by extracting the solid material resulting from the hydrolysis of rice starch.

Determination of Iodine Numbers and Amounts of the Fatty Acids.—Having the qualitative data, the amounts of the fatty acids were estimated[3] from the determinations of the iodine numbers[3] of the mixed and unsaturated fatty acids portions.

TABLE I

RESULTS OF DETERMINATIONS

Fatty acid sample	Mixed	Mixed	Unsaturated	Unsaturated
Weight, g.	0.1277	0.2558	0.1979	0.1664
Iodine number.	85.68	83.73	133.2	130.5

TABLE II

RESULTS OF DETERMINATIONS

Fatty acid	Palmitic	Oleic	Linolic
Percentage	36	35	29

Summary

The fatty acids (saturated and unsaturated) liberated by the hydrolysis of rice starch free from extraneous material have been identified and their amounts determined.

NEW YORK CITY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE ACETATE OF THE FREE ALDEHYDE FORM OF GLUCOSE

BY M. L. WOLFROM[1]

RECEIVED MARCH 12, 1929 PUBLISHED JULY 5, 1929

The formula of glucose is at present considered to be best represented by the closed chain or lactal type of structure. In the study of the reactivity of the sugars, there has frequently arisen a need for characterizing these compounds as open-chain hydroxy-aldehydes or ketones, capable of showing keto-enol tautomerism. This is particularly true in the study of their behavior in alkaline media, as exemplified by the work of Nef and his students, and by the work being conducted in this Laboratory by Evans and co-workers. Accordingly, we have attempted to isolate a crystalline derivative of the open-chain, free aldehyde form of glucose. We have succeeded in obtaining this as the acetate. This compound may be char-

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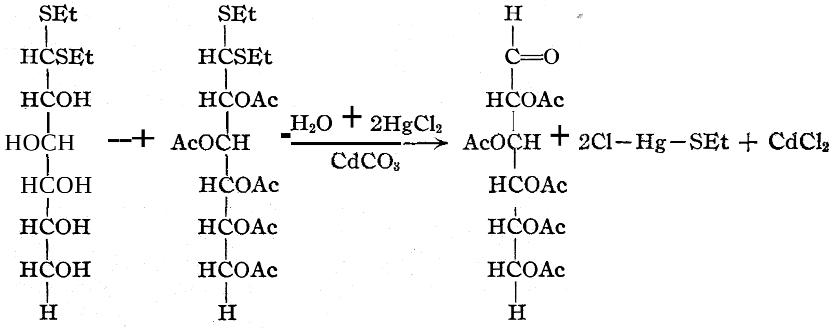
[13] Hertwig, Jamieson, Baughman and Bailey, *J. Assocn. Off. Agr. Chem.*, **8,** 439 (1925).

[1] National Research Fellow in Chemistry.

acterized as 2,3,4,5,6-penta-acetyl-*d*-glucose or, using the nomenclature proposed by T. M. Lowry[2] in considering the free aldehyde form as the intermediary in mutarotation, μ-*d*-glucose penta-acetate.

Emil Fischer[3] prepared the thio-acetal of glucose and of other aldoses. He showed that the thio-acetal groups could be removed with mercuric chloride and that the composition of the precipitate formed was Cl-Hg-S-Et. W. Schneider and J. Sepp[4] showed that under proper conditions one thio-acetal group could thus be removed, leaving the a-thio-glucoside. This procedure was improved by E. Pacsu.[5] Schneider and Sepp prepared the acetate of glucose-ethylmercaptal and unsuccessfully attempted to remove the thio-groups. We were unaware of this attempt at the time our experimental work was performed. P. A. Levene and G. M. Meyer[6] methylated glucose-diethylmercaptal and removed the thio-acetal groups with mercuric chloride, obtaining the 2,3,4,5,6-pentamethylglucose. They prepared its dimethyl acetal and extended the work to mannose and galactose.[7] Owing to the great difficulty of obtaining crystalline products in the methylated sugar series, all these compounds were obtained as distilled sirups.

By the employment of definite experimental conditions, we have succeeded in removing the thio-acetal groups from d-glucose-diethylmercaptal penta-acetate without de-acetylation. The steps involved are as follows



The resulting crystalline glucose penta-acetate differs in its characterizing constants from the two α-[8] and β-forms[9] known. It possesses a low optical rotation, as would be expected from its open-chain structure, and gives a definite Schiff aldehyde test. It dissolves in water on slight heating and

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[2] T. *M*. Lowry, *Z. physik. Chem., 130,* 125 (1928).

[3] E. Fischer, *Ber.,* 27,673 (1894).

[4] (a) W. Schneider and J. Sepp, *Ber.,* 49, 2054 (1916); (b) *ibid.,* 51, 220 (1918).

[5] E. Pacsu, *Ber.,* 58,511 (1925).

[6] P. A. Levene and G. M. Meyer, *J. Biol. Chem.,* 69,175 (1926).

[7] P. A. Levene and G. M. Meyer, *ibid.,* 74,695 (1927).

[8] Erwig and Koenigs, *Ber.,* 22, 1464, 2207 (1889).

[9] Tanret, *Bull. soc. chim.,* [3] 13,261 (1895).

reacts with semicarbazide to form a crystalline glucose-semicarbazone penta-acetate.

The free aldehyde form of glucose may be considered one of the important tautomeric phases of this compound. It is perhaps the intermediary in mutarotation phenomena.[2] Certainly it is the form first involved in enolic transformations. H. Kiliani[10] has recently called attention to the unimportance of the position of the oxygen bridge in many of the most important reactions of glucose, the end result being the same regardless of the type of ring assumed. The lactal structure may be considered as a passive tautomeric phase, opening, when required, to form the more reactive free aldehyde phase. Thus, the lactal form may be a device of nature for more nicely regulating the reactivity of the aldose or ketose molecule. The so-called y-ring forms, which are best characterized in the sugar acetate series, are known to possess the property of ease of lactal rupture. Their sensitivity to reagents may then be due to the ease of formation of the open-chain forms, the latter being the true reactive phases.

Further work on this compound and the extension of the reactions to other sugars is in progress.

Experimental

Preparation of Glucose-ethylmercaptal Penta-acetate.—A procedure different from that of W. Schneider and J. Sepp[4b] was employed. Five g. of glucose-ethylmercaptal (m. p. 127°) was dissolved at room temperature in 18 cc. of dry pyridine. The solution was cooled in ice and 36 cc. of acetic anhydride added gradually. A considerable amount of solid was thrown out of solution in a fine state of subdivision. It was kept at 0° with occasional shaking until the solid had redissolved, about ten minutes being required. The solution was allowed to stand overnight and was then gradually poured into a liter of ice water, with stirring. A sirup was formed which crystallized after standing in the ice box for about ten days. This was filtered and washed with cold water, 8.1 g. of product being obtained. This was recrystallized by dissolving in methyl alcohol, adding water to opalescence, nucleating and allowing to stand in the ice box. A sirupy phase was first formed which gradually crystallized in very good condition. Further portions of cold water were then added, a 97% recrystallization yield of pure product being possible.

After one recrystallization, the substance melted at 45–47° and showed $[\alpha]_D^{30} = +11.4°$ (0.4050 g. subs, 10.07 cc. of chloroform soln., $\alpha_D = +0.46°$, 1-dm. tube) in chloroform solution. After four recrystallizations, the m. p. was 45–47' and the rotation in chloroform solution was $[\alpha]_D^{29} = +11.2°$ (1.255 g. subs., 24.88 cc. of chloroform soln., $\alpha = +1.13°$, 2-dm. tube). A rotation in acetylene tetrachloride gave the value $[\alpha]_D^{28} = +17.4°$ (1.250 g. subs., 24.88 cc. of acetylene tetrachloride soln., a $= +1.75°$, 2-dm. tube). W. Schneider and J. Sepp[4b] give the melting point as 42–45° and $[\alpha]_D^{20} = +17.7°$ in acetylene tetrachloride.

2,3,4,5,6-Penta-acetyl-*d*-glucose.—An amount of glucose-ethylmercaptal penta-acetate (m. p. 45–47°) equal to 25.2 g. (1 mol.) was dissolved in 90 cc. of acetone and 45 cc. of water added. The clear solution was held in a 3-necked, round-bottomed flask provided with a reflux condenser and a mercury-sealed mechanical stirrer. An

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[10] H. Kiliani, *Z. angew. Chem.*, 42, 16 (1929).

excess, 45–50 g., of washed cadmium carbonate was added and under rapid stirring a solution of 49.5 g. (3.6 mols.) of mercuric chloride dissolved in 72 cc. of acetone was gradually added. Stirring was maintained at room temperature for twenty-four hours, with occasional additions of small amounts of fresh cadmium carbonate. At the end of this period the reaction flask was encased in a water-bath, and this rapidly heated to 50° and held at this temperature fifteen minutes, very vigorous mechanical stirring being maintained. The bath was then rapidly heated until refluxing began and the solution was refluxed gently for fifteen minutes. The solution was then filtered from the excess cadmium carbonate and CI-Hg-S-Et precipitate, an excess of fresh cadmium carbonate being placed in the suction flask, and the precipitate washed with acetone. The filtrate was then concentrated to dryness at 30–35° under reduced pressure and in the presence of excess cadmium carbonate. The residue was dried by repeatedly adding acetone and distilling under reduced pressure. The residue was extracted with warm chloroform, filtered, and the chloroform evaporated at room temperature in a vacuum desiccator. The crude product crystallized during the course of this evaporation. This was dissolved in 50 cc. of hot acetone, 25 cc. of alcohol-free ether added and then petroleum ether (40–60°) to opalescence. The substance crystallized out in plates. After standing for several hours in the ice box, the material was filtered, washed with a cold mixture of the same composition as the mother liquor and finally with petroleum ether. The amount of the product was 10.1 g., m. p. 116.5°. A further crop of 1.9 g. was obtained from the filtrate by the addition of more petroleum ether.

After one recrystallization the product melted at 116.5" and gave the value $[\alpha]^{25}_{\mathrm{D}} = +3.3°$ (1.244 g. subs., 24.88 cc. of acetylene tetrachloride soln., a $= +0.33°$, 2-dm. tube) in acetylene tetrachloride. After three recrystallizations performed in the same general way, the melting point was 119.5–120.5° and the polarization value in the same solvent was $[\alpha]^{26}_{\mathrm{D}} = +2.6°$ (0.4985 g. subs., 10.08 cc. of acetylene tetrachloride soln., a: $= +0.14°$, 1.1-dm. tube). After five recrystallizations the melting point was 116–118° and the polarization value in the same solvent was $[\alpha]^{25}_{\mathrm{D}} = +2.7°$ (0.5028 g. subs., 10.05 cc. of acetylene tetrachloride soln., $\alpha = +0.15°$, 1.1-dm. tube). A mixed melting point with pure 8-glucose penta-acetate (m. p. 131°, $[\alpha]^{25}_{\mathrm{D}} = +4.2°$, $CHCl_3$) gave the value 106–109°. In chloroform (U.S.P.) solution the values $[\alpha]^{24}_{\mathrm{D}} = -4.6'$ ($c = 4.997$) and $[\alpha]^{24}_{\mathrm{D}} = -4.8'$ ($c = 4.725$) were obtained. This value changed slowly to dextro, due probably to acetal formation with the ethyl alcohol present in the U.S.P. chloroform. In methyl alcohol the initial rotation was $[\alpha]^{25}_{\mathrm{D}} = +10°$ (c $= 4.980$; $c = 2.013$), changing slowly in the dextro direction. a-Glucose penta-acetate shows the melting point 113° and $[\alpha]^{20}_{\mathrm{D}} = +101.6°$ ($CHCl_3$), while 8-glucose penta-acetate possesses the melting point 132" and $[\alpha]^{20}_{\mathrm{D}} = +3.8°$ ($CHCl_3$).[11]

Anal. Subs., 0.2183: CO_2, 0.3947; H_2O, 0.1124. Subs., 0.2039: CO_2, 0.3697; H_2O, 0.1092. Subs., 0.0993: 12.7 cc. of 0.1 *N* KOH. Calcd. for $C_6H_7O_6(CH_3CO)_5$: C, 49.20; H, 5.69; cc. 0.1 *N* KOH, 12.7. Found: C, 49.31; H, 5.76; C, 49.45; H, 5.99; S, absent.

I am indebted to Professor W. J. McCaughey of the Department of Mineralogy of this University for the following crystallographic description of the compound.

"Crystal, monoclinic, tabular in direction parallel to side (clino) pinacoid. On the flat tabular face emerges an acute bisectrix; the optic angle is small, probably around 40°. On the clinopinacoid, the index of refraction of beta (β) and gamma (y) can be measured. Sometimes when crystalliza-

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[11] C. S. Hudson, *Scientific* Papers of *the Bureau* of Standards, No. 533, 379 (1926).

tion takes place from dilute solution, the crystals separate in elongated forms showing parallel extinction and negative elongation (elongation || to (a) alpha). With this orientation alpha (a) can be measured. The optical sign of the crystal is negative; the indices are a = 1.460, β = 1.500–, γ = 1.515.

"The vibration direction of beta (β) is inclined to what is taken to be crystallographic axis c by 1–2°. The vibration direction alpha is parallel to crystallographic axis $\bar{b}$. The crystal faces present are basal pinacoid, clinopinacoid, orthopinacoid and an orthodome. When the crystal habit shows growth in the direction of crystallographic axis $\bar{b}$ it appears as square prisms. When the crystal is tabular in the direction of $\bar{b}$ it shows hexagonal outline but the adjacent angles are not 120° as in a truly hexagonal crystal.

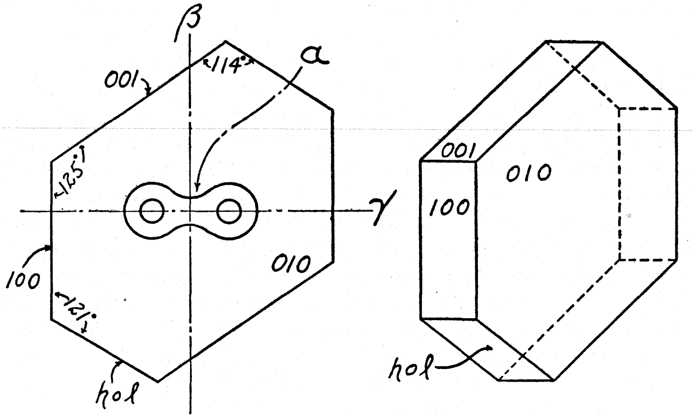

Fig. 1.—Crystalline form of μ-*d*-glucose penta-acetate, tabular habit.

The face having the hexagonal outline is the side or clinopinacoid. The size of the crystals was 0.2 mm.

"p-Glucose penta-acetate consists of needles showing parallel extinction and negative elongation. Indices: low = 1.47; high < 1.50."

The crystals of the new penta-acetate are very soluble in chloroform, soluble in acetone, alcohol and warm water, moderately so in ether and benzene and practically insoluble in petroleum ether (40–60°). The substance gave a positive fuchsin or Schiff aldehyde reaction. The fuchsin solution available gave a negative reaction with vanillin. With benzaldehyde a faint coloration was obtained at one minute and a distinct coloration at one and a half minutes. On dissolving 50–70 mg. of the acetate in about 0.5 cc. of warm acetone, cooling to room temperature, and adding 2.5 cc. of the reagent, a faint coloration was obtained at one and one-half to two minutes, becoming very distinct at five minutes. A blank on the acetone used gave negative results.

d-Glucose-semicarbazone Penta-acetate.—Four and one-half g. (1 mol.) of pure μ-glucose penta-acetate was dissolved in 45 cc. of warm water, cooled to room temperature, and a mixture of 1.1 g. of semicarbazide hydrochloride (0.9 mol.) and 1.8 g. of potassium acetate (1.6 mols) was added in the solid form. In a few minutes the solution became cloudy and an oil was gradually deposited. On standing overnight at room temperature this solidified. This was filtered and washed with cold water, 3.6 g. being obtained. The material was dissolved in methyl alcohol, treated with decolorizing carbon, filtered and water added. On standing at ice-box temperature 1.4 g. of crystals (m. p. 148–150°) in the form of minute elongated prisms was deposited. These were removed by filtration, washed with water and a further crop of 1 3 g (m. p. 148–150°) obtained from the filtrate by further addition of water. On two further recrystallizations the substance melted at 150–151° and on two more (5) melted at 150°.

Anal. Subs , 0.2055: N_2, 18.83 cc. (751.5 mm., 28°). Calcd. for $C_7H_{10}O_6N_3$-$(CH_3CO)_5$: N, 9.40. Found: N, 9.87. Calcd. for 0.2019: 22.6 cc. 0.1 *N* KOH. Found: 22.7 cc. Calcd. for 0.2074: 23.2 cc. 0.1 N KOH: Found: 23.1 cc.

The writer wishes to acknowledge his indebtedness to Professor W. L. Evans for his inspirational counsel and advice.

Summary

1. A new form of d-glucose penta-acetate has been prepared in pure condition.

2. Evidence is given that this compound possesses the open-chain, free aldehyde structure and the suggestion is made that the name μ-*d*-glucose penta-acetate be applied to the substance.

3. The crystalline semicarbazone of this aldehyde has been prepared in pure form.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF ILLINOIS]

PREPARATION OF SOME METHYLATED GALLIC ACIDS

BY R. L. SHRINER AND P. MCCUTCHAN

RECEIVED MARCH 13, 1929 PUBLISHED JULY 5, 1929

During the course of a study of some anthocyan pigments it was desired to have samples of certain methylated gallic acids, since these are produced by degradation of the anthocyanidin. The compounds desired were: 3,5-dimethylgallic acid, 3,4-dimethylgallic acid and 3-methylgallic acid. The first of these, syringic acid, is easily prepared by the method of Bogert and Ehrlich,[1] and its properties and derivatives[2] have been thoroughly studied. However, the data available in the literature on the other two methylgallic acids are very meager. The 3,4-dimethylgallic acid has been previously prepared by Zincke and Francke[3] and Her-

Bogert and Ehrlich, THIS JOURNAL, 41,798 (1919).

[2] Bogert and Coyne, *ibid.*, 51, 569 (1929).

[3] Zincke and Francke, *Ann.*, 293, 191 (1896).

zig and Pollak,[4] and 3-methylgallic acid by Vogl.[5] Since the methods used in the present work for the preparation of these last two compounds differed from those previously used and since the properties of the compounds obtained do not agree with those recorded in the literature, it was thought that a brief report of their preparation would be of interest.

Vanillin was the starting material for the preparation of both of these compounds. The 3,4-dimethylgallic acid was obtained as a result of the following series of preparations: Vanillin ⟶ 5-bromovanillin ⟶ 5-bromo-3,4-dimethoxybenzaldehyde ⟶ 5-bromo-3,4-dimethoxybenzoic acid ⟶ 3,4-dimethylgallic acid. The product crystallized from alcohol in long white needles and melted at 184–185°. Zincke and Francke[3] gave no melting point at all, while Herzog and Pollak[4] reported 189–192°. It was free from bromine and gave only a light yellow color with ferric chloride, which indicates the absence of gallic acid and 3-methylgallic acid which might be produced by the action of the alkali in the last step.

The 3-methylgallic acid was prepared from 5-bromovanillin by heating the latter with alkali and copper powder. After careful purification the 3-methylgallic acid was obtained in the form of needles which melted constantly at 131–132°. The previously reported value[8] was 199–200°. Dilute ferric chloride produced a light green color quite distinct from the blue produced by gallic acid itself.

Experimental

5-Bromovanillin.—A solution of 105 g. of bromine in 200 cc. of glacial acetic acid was added to 100 g. of vanillin dissolved in 200 cc. of glacial acetic acid. The bromovanillin separated at once. It was filtered off and recrystallized from 95% alcohol. Colorless cubic crystals which soon turned yellow on standing were obtained; yield, 118 g. or 77.6% of the theoretical. It melted sharply at 163–164°, which agrees with the melting point recorded by Dakin.[6]

5-Bromo-3,4-dimethoxybenzaldehyde.—A solution of 10.5 g. of 5-bromovanillin in 75 cc. of 2.5% sodium hydroxide solution was stirred vigorously and 10 cc. of dimethyl sulfate added. As soon as the solution became acid to litmus another 10 cc. of dimethyl sulfate was added with sufficient alkali to render the solution alkaline. In this manner four more successive portions of dimethyl sulfate were added, keeping the temperature between 45 and 50°. After the addition of the last portion the solution was boiled for two hours and then cooled. The methylated bromovanillin was filtered off and recrystallized from 80% alcohol. Nine g. (80% of the theoretical) of white flocculent crystals was obtained melting at 61–62°. This agrees with the value reported by Jones and Robinson.[7]

5-Bromo-3,4-dimethoxybenzoic acid.—A hot solution of 22 g. of potassium permanganate in 500 cc. of water was added with vigorous stirring to a boiling mixture of 30 g. of 5-bromo-3,4-dimethoxybenzaldehyde and 300 cc. of water containing 35 g. of potassium carbonate. After refluxing for one hour the solution was cooled and filtered.

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[4] Herzig and Pollak, Monatsh., 23, 704 (1902).

[5] W. Vogl, *ibid.*, 20, 395 (1899).

[6] Dakin, *Am. Chem. J.*, 42, 493 (1909).

[7] Jones and Robinson, *J. Chem. Soc.*, 111, 922 (1917).

The filtrate was acidified, the white precipitate filtered and recrystallized from hot water, yield, 30 g. of white crystals, m. p. 190–192°, which agrees with the melting point reported by Dakin.[6]

3,4-Dimethylgallic acid.—Ten g. of 5-bromo-3,4-dimethoxybenzoic acid, 200 cc. of 8% sodium hydroxide and 2 g. of copper powder were placed in an iron pipe fitted with lead-seated screw caps. The bomb was heated to 200° for one hour. After cooling the contents were acidified with dilute sulfuric acid and extracted with four 100-cc. portions of ether. The ether was distilled and the residue recrystallized from alcohol. Long colorless needles were obtained melting at 184–185°. Recrystallization from hot water or alcohol did not change the melting point. It gave a very light yellow color with ferric chloride; yield, 1.5 g. (20% of the theoretical).

Anal. Subs, 0.1118: CO_2, 0 2228; H_2O, 0 0520. Calcd, for $C_9H_{10}O_5$: C, 54.52. H, 5.09. Found: C, 54.45; H, 5 20.

The acetyl derivative was prepared by acetylation with acetic anhydride and a drop of perchloric acid according to the general method of Conant and Hall[8] The acetate was crystallized from alcohol. Needles melting at 137–138° were obtained

Anal. Subs., 0.0702: CO_2, 0.1415; H_2O, 0.0325. Calcd. for $C_{11}H_{12}O_6$: C, 55.00; H, 5.01. Found: C, 54.98; H, 5.18.

3-Methylgallic Acid.—The simultaneous removal of bromine and oxidation of the aldehyde group of 5-bromovanillin was accomplished by heating 5 g. of the latter with 100 cc. of 8% aqueous sodium hydroxide and 2 g. of copper powder at 200–210° for one hour. The reaction mixture was cooled, acidified with dilute sulfuric acid and extracted with ether. The ether was distilled and the residue treated with sodium bicarbonate solution. The insoluble material, consisting of unreacted 5-bromovanillin and some condensation products, was filtered and the filtrate acidified. The material which separated was recrystallized several times from benzene and melted sharply at 131–132"; yield, 1.0 g. Ferric chloride gives a light green coloration. It was acetylated by the method used above and the diacetate obtained after crystallization from benzene in the form of colorless plates melting at 102–103°.

Anal. Subs., 0.1621: CO_2, 0 3180; H_2O, 0 0654 Calcd. for $C_{12}H_{12}O_7$: C, 53.71; H, 4.52. Found: C, 53.50; H, 4.48.

Summary

The preparation and properties of 3,4-dimethylgallic acid and 3-methylgallic acid are described.

URBANA, **ILLINOIS**

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[8] Conant and Hall, THIS JOURNAL, 49,3047,3062 (1927).

[Contribution from the Chemical Laboratory of the College of Liberal Arts, Northwestern University]

MERCURATION IN ALKALINE SOLUTION. PRELIMINARY PAPER

By A. L. Fox with Frank C. Whitmore

Received March 15, 1929 Published July 5, 1929

Mercuration is ordinarily carried out by means of mercuric acetate in a solution acidified with acetic acid. When 2,3-hydroxynaphthoic acid was mercurated in this way, the mixture was tested with sodium hydroxide to detect any unreacted inorganic mercury. It was found that rapid addition of sodium hydroxide gave a precipitate of mercuric oxide but that slow addition did not do so. After some study it was found that the addition of the base was increasing the speed of mercuration. It was finally found that 2,3-hydroxynaphthoic acid could be mercurated in strongly alkaline solution. This method of mercuration was applied successfully to salicylic acid and to phenol. It failed when applied to *m*-hydroxybenzoic acid, p-hydroxybenzoic acid, a-naphthol, o-nitrophenol, aniline, anthranilic acid, sulfanilic acid, benzenesulfonic acid, 1-naphthoic acid and phthalic acid. It should be noted that traces of mercuration products may have been formed but none could be isolated using the same technique which gave good yields with 2,3-hydroxynaphthoic acid, salicylic acid and phenol.

The mercuration product obtained by this method from phenol corresponded to an anhydro-hydroxymercuriphenol.

Experimental Part

Mercuration of **2,3-Hydroxynaphthoic** Acid in Alkaline Solution.—A solution of 30 g. (0.16 mole) of the acid in 500 cc. of water and 150 cc. (0.9 mole) of 6 N sodium hydroxide was heated to boiling and stirred during the gradual addition of 52 g. (0.16 mole) of mercuric acetate dissolved in 300 cc. of water and 10 cc. (0.15 mole) of acetic acid. As the mercuric acetate solution was added a momentary precipitate of mercuric oxide formed. The mixture was boiled for a few minutes, treated with decolorizing carbon, filtered and treated with a slight excess of sodium chloride and slightly less than enough dilute hydrochloric acid to make the mixture acid. The precipitate was dried. It formed a yellow powder which was probably anhydro-4-hydroxymercuri-3-hydroxy-2-naphthoic acid.

Anal. Calcd. for $C_{11}H_6O_3Hg$: Hg, 51.9. Found: 51.8, 51.4.

The mercuration was repeated with cold dilute solutions with similar results.

Mercuration of Salicylic **Acid.**—This mercuration was carried out in an exactly similar way. From 15 g. of salicylic acid was obtained 27 g. of hydroxymercurisalicylic acid.

Anal. Calcd. for $C_7H_6O_4Hg$: Hg, 56.6. Found: 57.0, 56.8.

Mercuration of **Phenol.**—This process was similar to the other two, 100 g. of phenol yielding 215 g. of anhydro-hydroxymercuriphenol.

Anal. Calcd. for C_6H_4OHg: Hg, 68.6. Found: 68.9.

A similar mercuration of phenol using mercuric chloride instead of the acetate gave the same product

Unsuccessful Attempts at Mercuration in Alkaline Solution. **α-Naphthol** was oxidized immediately by this procedure. Similar results were obtained with aniline.

o-Nitrophenol.—On adding mercuric acetate solution to a boiling alkaline solution of o-nitrophenol a permanent precipitate of mercuric oxide formed. The experiment was discontinued. Similar results were obtained with anthranilic acid, sulfanilic acid, benzenesulfonic acid, 1-naphthoic acid and phthalic acid.

Summary

It has been found that certain organic compounds can be mercurated in alkaline solution while other compounds of very similar structure cannot.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD, UNIVERSITY OF ST. ANDREWS]

THE MOLECULAR STRUCTURE OF INULIN. ISOLATION OF A NEW ANHYDROFRUCTOSE

BY JAMES COLQUHOUN IRVINE AND JOHN WHITEFORD STEVENSON

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The first researches designed to investigate the molecular structure of inulin with the precision rendered possible by the methylation method were carried out by Irvine and Steele.[1] These authors showed that the polysaccharide although converted by hydrolysis into the normal levorotatory form of fructose is actually based on the unstable dextrorotatory variety of the hexose known as γ-fructose. The research was subsequently extended[2] to include a more detailed examination of dimethyl- and trimethylinulin, together with the dimethyl- and trimethylfructoses obtained, respectively, from these derivatives by hydrolysis.

The collective evidence, although complicated by a number of minor irregularities such as the tendency of trimethylinulin to undergo depolymerization from a levorotatory powder to a dextrorotatory sirup, pointed to the idea that the molecule of inulin is symmetrical in the sense that all of the fructose residues belong to the γ-type and that in each fructose residue three hydroxyl groups occupy the same positions. This view was based on the fact that on hydrolysis trimethylinulin gave a homogeneous trimethyl-7-fructose, and all subsequent speculations on the structure of inulin have been founded on this observation. In the course of the past five years we have, however, accumulated much incidental evidence that the inulin problem is not so simple as at one time appeared, and we have accordingly continued our investigations; in the meantime Haworth has published what is, in effect, a repetition of our earlier work,

[1] Irvine and Steele, J. Chem. *Soc.*, 117, 1474 (1920).

[2] Irvine, Steele and Shannon, *ibid.*, 121, 1060 (1922).

contributing, however, the new observation that our trimethyl-7-fructose is capable of yielding a phenylosazone.[3] Lest the idea should prevail that the molecular structure of inulin is now fully solved, it is advisable to contribute some results which show that such is not the case.

The first indication that the molecular unit of inulin is not homogeneous is found in the results of Irvine and Steele. The sequence of reactions

$$\text{Inulin} \longrightarrow \text{Trimethylinulin} \longrightarrow \text{Trimethyl-}\gamma\text{-fructose}$$

proceeded smoothly, giving good yields at each stage, but the yield of sugar, relative to the weight of trimethylinulin from which it is formed, was invariably of the order of 80%. The loss of 20% is accounted for by the fact that in the purification of the sugar by distillation a small first fraction, consisting of a mobile sirup, was collected. This constituent is now being examined in detail and we have traced its origin to the existence in inulin of at least one component yielding an anhydro-fructose of an unknown type. The new anhydro-sugar can be prepared from inulin in various ways, all of which emphasize its stability. For example, when triacetylinulin is dissolved in chloroform containing fuming nitric acid, the anhydro-ring of most of the fructose residues is opened and from its properties the essential product appears to be a triacetylfructose dinitrate. The reaction is therefore analogous with that studied by Oldham,[4] who converted triacetylglucosan into triacetylglucose-1,6-dinitrate by similar processes. On treating the crude triacetylfructose dinitrate with methyl alcohol, conversion into triacetylmethylfructoside mononitrate took place and a crop of crystals separated which amounted to approximately 20% by weight of the triacetylinulin initially taken. The product, which crystallized in needles melting at 123° and showed $[\alpha]_D + 1.5°$ in chloroform, was a triacetylanhydrofructose. As was to be expected, this acetate of anhydrofructose is devoid of action upon Fehling's solution but, unexpectedly, the anhydro-ring proved to be unusually stable, being opened only by prolonged heating with acids.

On removing the acetyl groups by the action of dimethylamine, the parent anhydrofructose separated in spheroidal crystals melting at 143–145° and showing $[\alpha]_D + 30.17°$ in water. It is significant that although the new anhydro-sugar can be hydrolyzed to give normal fructose in almost quantitative amount, it is much more stable than the known derivatives of γ-fructose. For example, although heating with $N/100$ hydrochloric acid effects the rapid hydrolysis of sucrose and likewise converts about 80% of inulin into fructose, the same reagent has little effect in opening the anhydro-ring of the particular form of anhydrofructose now under consideration. The importance of this observation will be referred to later.

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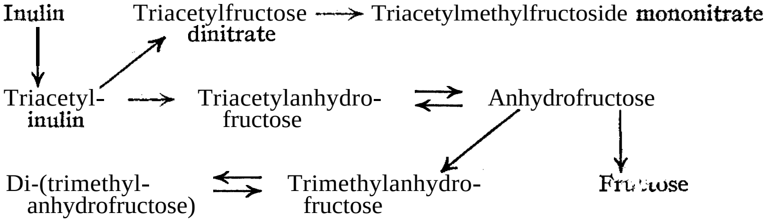
[3] Drew and Haworth, *J. Chem. Soc.*, 133,2690 (1928).

[4] Oldham, *ibid.*, 127, 2840 (1925).

In order to gain an insight into the structure of the anhydrofructose, the compound was subjected to the methylation process, it being found necessary to supplement the methyl sulfate reaction by treatment with silver oxide and methyl iodide. The product proved to be a di-(trimethylanhydrofructose) showing that either the methylation, or more probably the vacuum distillation necessary to isolate the compound, had occasioned polymerization. This is not an abnormal experience in the case of methylated fructoses and, as is usual with polymers of low molecular weight in the inulin series, the rotation was dextrorotatory ($[\alpha]_D + 23.8°$). By employing the general method of diminishing polymerization by heating with methyl alcohol containing hydrogen chloride, the above dimeride was converted into the monomeric form of trimethylanhydrofructose, the structural study of which is now in progress.

The scheme of reactions involved in the research is represented below.



Discussion

In the particular method of preparing the anhydro-fructose now described, the possibility must not be overlooked that the use of a powerful reagent such as nitric acid may cause intramolecular changes in triacetylinulin, thereby forming triacetyl-anhydrofructose as an adventitious product. This possibility is ruled out as, when triacetylinulin is hydrolyzed by acetic acid containing 0.03% of sulfuric acid, the same triacetyl-anhydrofructose can be isolated from the products. Moreover, when inulin is subjected to graded acetolysis by Barnett's method,[5] 18% of the polysaccharide fails to pass into solution and triacetyl-anhydrofructose is obtained from this stable fraction. The accumulated evidence[6] is thus in favor of the idea that inulin is not homogeneous but consists of at least two main components one of which is easily hydrolyzed while the other is relatively resistant to hydrolytic agents. These components fall into two classes present in the approximate ratio of 4:1 and for the time being, it is not safe to claim that more than 80% of the inulin aggregate is based on y-fructose. It is possible that the remainder may also be derived from y-fructose but in such an event the anhydro-ring must occupy a more stable position than in the major component of the polysaccharide; alternatively,

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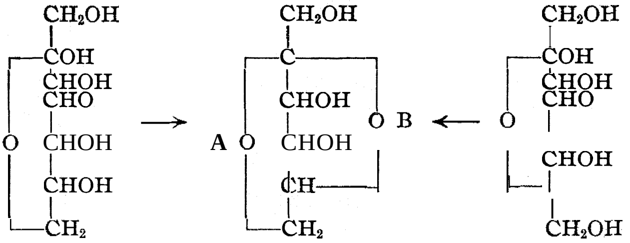
[5] Barnett, J. *Soc.* Chem. *Ind.*, 40, 8T (1921).

[6] See also Irvine, Oldham and Skinner, THIS JOURNAL, 51, 1279 (1929).

this constituent may be related to normal fructose or to an isomeric form of the ketose hitherto unknown.

It will at once be evident that a serious complication is introduced into the constitutional study of inulin, as the lack of homogeneity now revealed may be due to several causes. For example, inulin may be a polymeride of individual anhydrofructoses differing from each other, or it may be a polymeride of condensed fructose residues in which the structure of some of the C_6 units differs from that of others. This does not exhaust the possibilities, but until our structural examination of triacetyl-anhydrofructose is complete it is premature to develop the situation further or to utilize constitutional formulas in illustration. Obviously the solution of the inulin problem now demands a critical study of the relative stability of oxygen rings in the fructose series and also of methods whereby anhydro-sugars can be referred to their parent type. Thus, the anhydrofructose now under discussion might originate in either normal fructose or in γ-fructose and, in turn, the anhydro-ring may occupy the butylene-oxide or the amylene-oxide position. This is shown below.



Two oxygen-rings (A and B) are present in the anhydride and it is impossible to designate one as the anhydro-ring and the other as the oxygen-ring characteristic of the sugar. Nor is it always possible to identify which ring is opened during hydrolysis and which one is unaffected. Research on this problem is well advanced and the results will be applied in a further discussion on the structure of inulin to be communicated later.

Experimental

Action of Nitric Acid on **Triacetylinulin.**—The inulin employed was obtained from four different sources but no variation was found either in the composition or in the yields of the various products. Pringsheim's method was used for the preparation of inulin triacetate, the crude product being purified by dissolving in hot alcohol and pouring the solution into a large excess of water; all the specimens employed in the subsequent experiments were analyzed and conformed to the following standard: m. p. 97"; $[\alpha]_D = -33.9$" in chloroform and $-37.1°$ in glacial acetic acid (c = 2.6 in each case).

Numerous preliminary trials were necessary in order to ascertain the best conditions under which triacetylinulin is acted on by nitric acid. Using chloroform as the solvent, the addition of nitric acid up to 20% caused an alteration in the rotation from levo to dextro, but the product nevertheless consisted chiefly of unchanged triacetylinulin.

When the acid concentration was raised in successive experiments to 70% the dextrorotation of the liquid increased to the maximum, +48.8°, but the yield of product was then seriously diminished. Ultimately, a 30% solution of nitric acid in chloroform was selected as the most suitable reagent and the course of the reaction was followed polarimetrically, the results showing that the action was complete in thirty minutes, when the rotation had attained the value $[\alpha]_D$ +34°.

Triacetyl-anhydrofructose.—The conditions established above were used as the basis of the preparation of triacetyl-anhydrofructose but it was found advisable to carry out the preparation in successive experiments with small quantities of material. Five grams of well-dried triacetylinulin was dissolved in 70 cc. of chloroform and 30 cc. of fuming nitric acid (sp. gr., 1.55) added. The flask was stoppered and cooled, as heat is developed in the course of the reaction, and, from time to time, phosphorus pentoxide was added to remove traces of water. After thirty minutes the clear solution was poured into a separating funnel containing 200 cc. of water mixed with ice and shaken until all coloring matter had passed into the aqueous layer, the chloroform being then run off and dried over anhydrous sodium sulfate. A small quantity of barium carbonate was added to the filtered liquid, after which the solvent was distilled, fresh chloroform added, the solution again filtered and taken to dryness, the process being completed at 100° under diminished pressure. In this way 4.5 g. of a mobile sirup was obtained showing $[\alpha]_D$ +22° in chloroform for $c = 2.28$. As explained in the introduction, analysis showed this material to be a mixture consisting essentially of triacetylfructose dinitrate and triacetyl-anhydrofructose, the former constituent being convertible into the corresponding triacetylmethylfructoside mononitrate by boiling a 10% solution in methyl alcohol in the presence of barium carbonate.

When the sirup was dissolved in hot absolute alcohol the solution slowly deposited crystals, the weight of which was remarkably uniform in different experiments and amounted to 20% of the sirup taken. After recrystallization from absolute alcohol and drying at 100°, a pure product was obtained, but, considering the origin of the material, it was desirable to carry out a careful analytical survey. Nitrogen and ethoxyl were absent, no double bond was present, and the action of Fehling's solution was negative until after drastic hydrolysis. Analysis showed that the crystals contained half a molecule of combined acetic acid.

Anal. Calcd. for $C_{13}H_{18}O_9$: C, 49.05; H, 5.66; CH_3CO, 47.3. Found: C, 49.15, 48.99; H, 5.86, 5.90; CH_3CO, 46.1.

Difficulty was experienced in confirming the molecular weight. Using the cryoscopic method and employing benzene as a solvent, the mean of four experiments was 438, a value which indicates molecular association. In glacial acetic acid the freezing point depressions were irregular, but the molecular weight averaged 299, thus corresponding with a monomolecular form (calcd. for $C_{12}H_{16}O_8$, 288; for $C_{13}H_{18}O_9$, 318). Triacetylanhydrofructose crystallizes from alcohol in needles melting at 123". The compound, which is readily soluble in organic solvents generally and in hot water, is practically inactive, $[\alpha]_D$ +1.5" in chloroform for $c = 2.272$.

Anhydrofructose.—This preparation was likewise carried out in a succession of small-scale experiments. Five grams of triacetyl-anhydrofructose was added to 25 cc. of dry methyl alcohol containing 5% of dimethylamine. On shaking in the cold for twenty minutes the material passed into solution and the solvent was thereafter removed under diminished pressure, the residue being dried by raising the temperature slowly to 100°. The product consisted of a clear deliquescent glass weighing 2.6 g. and on dissolving in absolute alcohol and adding a few drops of dry ether a crystalline precipitate separated which was washed with ether–alcohol and finally with ether.

The anhydrofructose thus obtained forms transparent spheroidal crystals melting at 143–145°, is highly hygroscopic and fails to reduce Fehling's solution. In water, for $c = 2.32$, $[\alpha]_D = +30.17°$, but it is difficult to guarantee these constants in view of the hygroscopic character of the compound and in consideration of the fact that analysis disclosed the presence of a trace of acetyl.

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.44; H, 6.17; CH_3CO, nil; mol. wt., 162. Found: C, 44.49; H, 6.28; CH_3CO, 1.0; mol. wt. by the freezing-point method in water, 162.

The properties of anhydrofructose are simple. When acetylated under standard conditions it is reconverted almost quantitatively into the original triacetyl-anhydrofructose melting at 123° and showing $[\alpha]_D$ +1.5° in chloroform. The opening of the anhydro-ring of anhydrofructose was effected by heating at 100° a 2.5% solution of the substance in water containing 3% of oxalic acid, a polarimetric record of the reaction showing that the initial specific rotation of +25.7° altered regularly to the constant value −87.7°, so that the figures plotted on a smooth curve. This corresponds to a nearly quantitative conversion into normal fructose and, on working up the product in the usual manner, the sugar crystallized and was thereafter converted into glucose phenylosazone showing the correct constants.

Methylation of Anhydrofructose.—A preliminary methylation, carried out by means of methyl sulfate and sodium hydroxide, gave a partly alkylated product which was extracted with boiling alcohol and recovered. After three subsequent methylations with the same reagents, but using chloroform as the extracting agent, a quantitative yield of a transparent fairly mobile sirup was obtained which, when distilled at 206° (0.35 mm.) showed $n_D = 1.4731$ and gave a methoxyl content of 43.2%. The methylation was accordingly completed by dissolving the sirup in excess of methyl iodide and boiling with dry silver oxide, the extracting agent in this case being ether. The product, isolated in the customary manner, boiled at 166° (0.1 mm.); examination showed that the refractive index remained at 1.4730 but the methoxyl content had increased to the theoretical value.

Anal. Calcd. for $C_9H_{16}O_5$: C, 52.94; H, 7.84; OCH_3, 45.58. Found: C, 52.74; H, 8.14; OCH_3, 45.68.

When again distilled and collected in two equal fractions, the same constants and analytical composition were duplicated, so that the material was a homogeneous pure specimen of trimethylanhydrofructose. The specific rotation in chloroform for c = 2.5 was +23.8°. In view of the high boiling point, the value of the refractive index and the viscosity of the sirup, the compound had evidently undergone polymerization to some extent and, in an attempt to effect depolymerization, a solution was prepared in dry methyl alcohol containing 0.5% of dry hydrogen chloride and heated at the boiling point of the solvent. The specific rotation, initially +33.5°, increased steadily to the constant value +48.7°, which was attained in 150 minutes. After neutralizing with barium carbonate and isolating the product in the usual manner, a low-boiling mobile fraction was obtained which still retained the composition of a trimethyl-anhydrofructose, but the refractive index had altered to 1.4610, a value which corresponds to a monomeric form. Nevertheless, the depolymerization was incomplete, as higher-boiling fractions identical with the original material were also collected. These results show that the action of acid methyl alcohol had effected depolymerization but that, as is frequently the case in the methylated fructose series, molecular association was induced by distillation.

The authors desire to express acknowledgment to the Carnegie Trust for the Universities of Scotland for a Research Scholarship awarded to one of them.

Summary

1. When triacetylinulin is dissolved in chloroform and acted on by nitric acid the greater part of the material is converted into triacetylfructose dinitrate, the esterification being preceded by the opening of the anhydro-linkages.

2. One component of triacetylinulin present to the extent of 20% is resistant to the hydrolytic action and is isolated as triacetyl-anhydrofructose (m. p. 123°; $[\alpha]_D + 1.5°$ in chloroform). The same compound can be obtained in similar yield from other reactions in which triacetylinulin is used as the starting material.

3. Anhydrofructose (m. p. 143–145°; $[\alpha]_D + 30.17°$ in water) has been prepared from the triacetate by the action of dimethylamine. The compound is quantitatively convertible into fructose but is much more stable toward hydrolysts than the known derivatives of γ-fructose.

4. Anhydrofructose has been converted into trimethyl-anhydrofructose, which was isolated in a dimeric form.

5. The main conclusion drawn is that inulin is not related exclusively to a single form of γ-fructose but contains two classes of components in the approximate ratio of 4:1. Of these, one is relatively much more stable toward hydrolysis. The additional complication introduced into the constitutional study of inulin through these results is discussed.

UNIVERSITY OF ST. ANDREWS, SCOTLAND

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE ETHYL GASOLINE CORPORATION]

THE VAPOR PHASE OXIDATION OF ISOMERIC OCTANES. II. OCTANES WITH BRANCHED CHAINS

BY J. C. POPE, F. J. DYKSTRA AND GRAHAM EDGAR

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I. Introduction

In Part I of this paper[1] data were presented on the vapor phase oxidation of n-octane, which indicated that under the conditions in question the oxidation proceeds almost entirely according to certain simple reactions. These reactions are: (1) the formation of octaldehyde; (2) the oxidation of octaldehyde to carbon monoxide, water and aldehydes of successively smaller number of carbon atoms; and (3) a side reaction in which octaldehyde is oxidized to carbon dioxide, water and aldehydes of successively smaller number of carbon atoms.

In Part II data are presented on the vapor phase oxidation of five isomeric octanes, 3-methylheptane, 3-ethylhexane, 2-methyl-3-ethylpentane, 2,5-dimethylhexane and 2,2,4-trimethylpentane. These data were ob-

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[1] Pope, Dykstra and Edgar, THIS JOURNAL, 51, 1875 (1929).

tained in the course of a general survey of the oxidation characteristics of hydrocarbons, and are consequently somewhat fragmentary in nature. In three of the five cases only a single experiment was carried out, and the temperature range covered was not always as great as could be wished. Nevertheless, the data, when taken in conjunction with the much more detailed study of *n*-octane, seem to throw much light on the oxidation characteristics of branched-chain hydrocarbons, about which no information has been available heretofore, and it has been thought wise to publish them in their present form, since circumstances have prevented this Laboratory from carrying out the work more exhaustively.

The data are of especial interest in connection with the behavior of these hydrocarbons as fuels in the internal coinbustion engine, a subject which will be discussed in Part III of this paper.

II. Apparatus and Experimental Methods

(a) General.—The apparatus and experimental procedure were identical with those described in Part I. The runs were made with slowly rising temperature, except in the case of 2,5-dimethylhexane, in which several runs under constant temperature conditions were carried out.

(b) Materials.—The hydrocarbons were synthesized in this Laboratory by methods analogous to those described for the isomeric heptanes,[2,3] with the exception of 2,2,4-trimethylpentane, which was synthesized by the method described by Edgar.[4] The boiling points indicated a fair state of purity and were as follows: 3-methylheptane, 117.5–120.5°; 3-ethylhexane, 116–119°; 2-methyl-3-ethylpentane, 113–116°; 2,5-dimethylhexane, 108–110°; 2,2,4-trimethylpentane, 99.2–99.4°.

III. Experimental Data

(a) General.—The experimental data are expressed graphically in Figs. 1, 2, 3, 4 and 5, in which the oxygen consumed and the carbon oxides formed per mole of octane input are plotted against the temperature. As in the case of n-octane, the temperatures are the average values for the few degrees temperature range during sampling. The oxygen–fuel ratios were not always the theoretical values for complete combustion (12.5 moles O_2 to 1 mole octane), but they were usually not far from this value. The actual values are given in the figures.

(b) Individual Cases.—Before discussing the data it seems desirable to point out certain facts in connection with the behavior of the individual hydrocarbons. It will be recalled that in the case of n-octane, two abrupt changes in the nature of the reaction occurred, each involving luminescence

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[2] Edgar, Calingaert and Marker, THIS JOURNAL, 51, 1483 (1929).

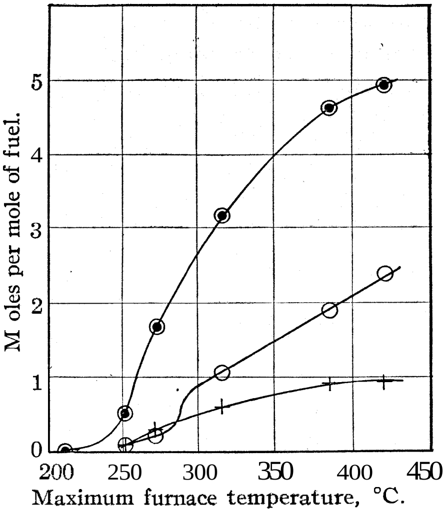
[3] The authors are indebted to Dr. J. W. McKinney and Mr. R. E. Marker for the actual preparations.

[4] Edgar, *Ind. Eng. Chem.*, 19, 145 (1927).

and strong pulsations in the oxygen and nitrogen flowmeters. The first of these was considered to be due to the incidence of a "chain" reaction involving the oxidation of an aldehyde to carbon monoxide, another aldehyde and water; the second, occurring at much higher temperatures, involved complete oxidation of all products to carbon dioxide and water. For the sake of convenience these phenomena will be referred to as "low temperature disturbance" and "high temperature disturbance," respectively.

In the case of 3-methylheptane and 3-ethylhexane low-temperature disturbances, similar to those of *n*-octane, were observed, occurring between temperature ranges of 280–305 and 285–302°, respectively. In the other three cases the low temperature disturbance was not observed.

The high-temperature disturbance was observed in the cases of 3-ethyl-hexane, 2-methyl-3-ethylpentane and 2,2,4-trimethylpentane, occurring at 510,526 and 560°, respectively. In the other two cases, the temperatures were not carried high enough for such disturbances to occur, but judging from the behavior of many hydrocarbons studied by this Laboratory, this phenomenon would undoubtedly have occurred had the temperatures been carried high enough.



●, O_2 reacted; ○, CO produced; +, CO_2 produced.

Fig. 1.—3-Methylheptane (oxygen/fuel ratio = 9.6/1).

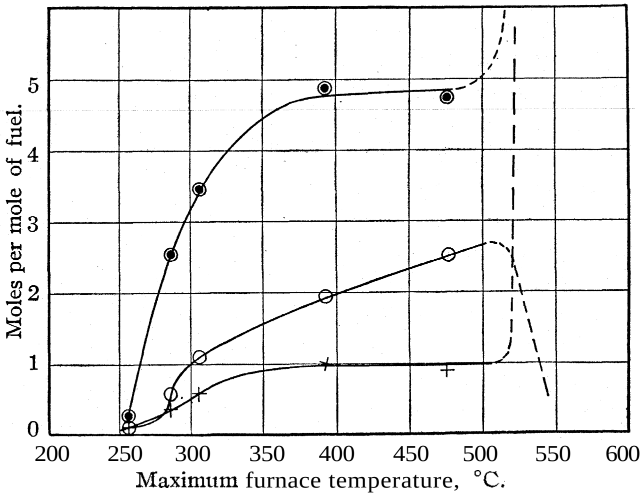
As in the case of n-octane, the low temperature disturbance was accompanied by an increase in the rate of formation of carbon monoxide, and the high-temperature disturbance by complete reaction to carbon dioxide and water.

NOTE.—In the case of 2-methyl-3-ethylpentane an experimental point was obtained at 431° in which very much less oxidation had occurred than at somewhat lower temperatures. A negative temperature coefficient of reaction is frequently observed in reactions of the type studied, but in the case in question the drop in the reaction rate is so pronounced as to suggest experimental error, such as might be caused by a temporary clogging of the fuel feed, or leakage of air into the sampling tube. There was no evidence of such occurrence, but it has been thought advisable to regard this experimental point as of doubtful significance when unverified by other determinations, and the curve has been drawn accordingly.

In the case of 2,5-dimethylhexane, the data refer to a series of constant temperature runs, rather than rising temperature runs, as in the other cases. Judging from the authors' experience with n-octane these data should, however, be reasonably comparable with the others.

IV. Discussion of Data

(a) General.—It might be expected that differences in resistance to oxidation would exist among these hydrocarbons, but no previous data are available to suggest the course of the reaction in such cases. It has been indicated by Stephens,[5] in the case of aromatic hydrocarbons with aliphatic side chains, that the oxidation of such hydrocarbons begins at a secondary carbon atom, but the nature of the hydrocarbons and the experimental conditions were so different from those involved in the present investigation as to make his conclusions of doubtful applicability.



◉, O_2 reacted; ○, CO produced; +, CO_2 produced.

Fig. 2.—3-Ethylhexane (oxygen/fuel ratio = 12.6/1).

Inspection of Figs. 1, 2, 3, 4 and 5 shows that distinct differences actually exist in the behavior of the different hydrocarbons. With the exception of the data for 2,2,4-trimethylpentane, the various curves show a marked similarity in general nature to those for n-octane (Part I), the oxygen consumpti-on curves, for example, rising rather abruptly at temperatures below 300" and then showing little further rise over a considerable temperature range. The extent to which oxidation proceeds, however, before the reaction slows down, varies greatly among the different hydrocarbons. 2,2,4-Trimethylpentane shows characteristics differing from the others. The significance of these variations will be discussed below.

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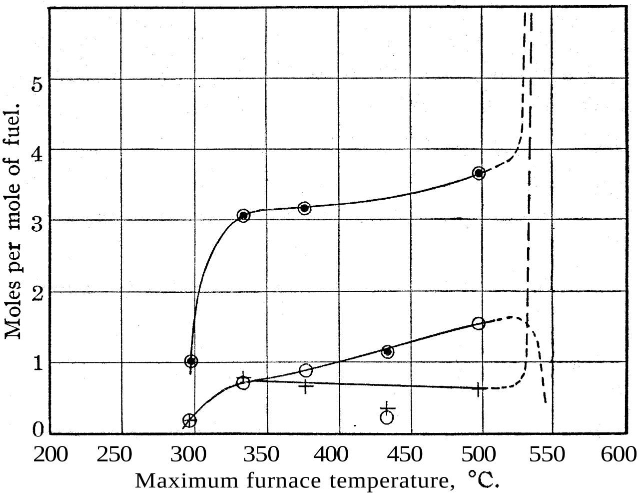
[5] Stephens, **This journal,** 50, 2523 (1928).

Although the data are not as complete as could be wished, it seems desirable to subject them to careful scrutiny in order to determine if possible (1) whether the reaction mechanism is similar to that of n-octane, and (2) the point of initial attack. These two questions will, therefore, be considered in order.

(b) Main Course of Reaction.—In the case of n-octane it was found that the total oxygen consumption per mole of octane input (at temperatures below the high-temperature disturbance) was very nearly equal to the total of one mole (to form an aldehyde), plus the number of moles of carbon monoxide (since the oxidation of an aldehyde to 1 mole of carbon monoxide, water and another aldehyde requires one mole of oxygen), plus 1.5 times the number of moles of carbon dioxide (since the oxidation of an aldehyde to carbon dioxide, water and another aldehyde requires 1.5 moles of oxygen), indicating that no other reactions than those suggested were occurring to an appreciable extent. Calculations on a similar basis for the four isomeric octanes, which are oxidized at low temperatures, give the results in Table I.



◉, O_2 reacted; ○, CO produced; +, CO_2 produced.

Fig. 3.—2-Methyl-3-ethylpentane (oxygen/fuel ratio =11.7511).

The experimental data for oxygen reacted agree reasonably well in most cases with those calculated, suggesting that the mechanism of oxidation is analogous to that of n-octane. The oxygen consumed is usually slightly greater than that calculated, indicating that a small amount of oxygen may have reacted to form olefins (small amounts of gas absorbable in fuming sulfuric acid were found experimentally) or some products other than those involved in the theory, but such reactions cannot be a major factor in the

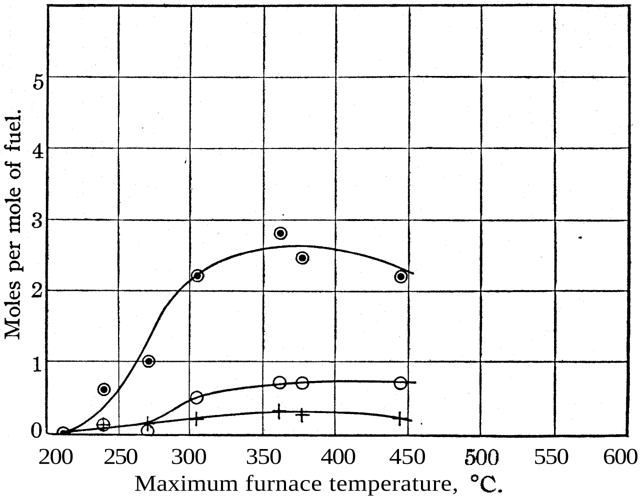
TABLE I

RESULTS OF CALCULATIONS

Moles of CO	Moles of CO_2	Moles of O_2 consumed	(1 + CO + 1.5 CO_2)	Moles of CO	Moles of CO_2	Moles of O_2 consumed	(1 + CO + 1.5 CO_2)
	3-Methylheptane				2-Methyl-3-ethylpentane		
0.2	0.3	1.65	1.65	0.75	0.8	3.05	2.95
1.1	.6	3.2	3.0	.90	.65	3.20	2.90
1.9	.9	4.6	4.25	.20	.3	1.15	1.65
2.4	.95	4.9	4.85	1.55	.60	3.70	3.45
	3-Ethylhexane				2,5-Dimethylhexane		
0.6	0 35	2.55	2.15	0.50	0.2	2.2	1.80
1.1	.6	3.45	3.0	.7	.30	2.80	2.15
1.95	1.0	4.90	4.45	.7	.25	2.45	2.07
2.5	.9	4.75	4.85	.7	.2	2.20	2.00

Data for 2,2,4-trimethylpentane are not included since it does not exhibit the low-temperature oxidation phenomena shown by the others.

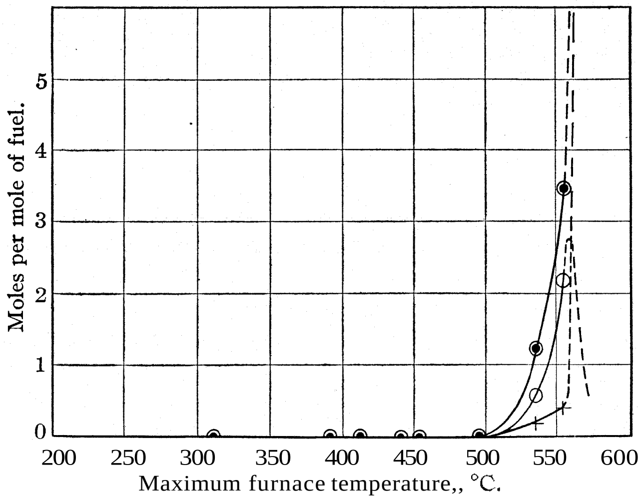
oxidation, since nearly all of the oxygen consumed is accounted for on the hypothesis outlined above. It seems reasonable, therefore, to assume for the four cases cited that, as in the case of n-octane, the primary product of oxidation is an aldehyde; that this aldehyde is further oxidized (a) by a "chain" reaction producing aldehyde, carbon monoxide and water and (b) by a reaction producing aldehyde, carbon dioxide and water; and that these reactions proceed until products are formed which resist further oxidation until temperatures are reached which are high enough for general disintegration to occur, accompanied by complete oxidation to carbon dioxide and water.



◉, O_2 reacted; O, CO produced; +, CO_2 produced.

Fig. 4.—2,5-Dimethyhexane (oxygen/fuel ratio = 9.1/1).

(c) Point of Initial Attack.—The data in the preceding paragraph indicate that the point of initial attack is a methyl group, rather than a secondary or tertiary atom. This view is substantiated by several facts: (1) the over-all similarity of the oxidation curves to that of n-octane and the similar phenomena observed during the reaction; (2) the hydrocarbons containing secondary or tertiary atoms are more resistant to oxidation than those not containing them, and the more highly condensed the structure, the more resistant the hydrocarbons become; **(3)** oxidation of secondary carbon atoms would be expected to result in a rapid degradation of the hydrocarbon into molecules of low molecular weight, which would be oxidized with difficulty even in the form of aldehydes (see Part I). The result of such reactions would be a large consumption of oxygen without production of correspondingly large amounts of carbon oxides, which is contrary to the experimental data. It appears, therefore, that secondary and tertiary atoms are points of strength rather than weakness, and that the initial attack is at a methyl group, as in the case of n-octane. With n-octane, however, only the methyl groups at the ends of the molecule are available for oxidation. In the case of most of the isomeric octanes the initial attack might theoretically be at any one of several points.



◉, O_2 reacted; O, CO produced; +, CO_2 produced.

Fig. 5.—2,2,4-Trimethylpentane (oxygen/fuel ratio = 12.3/1).

Examination of Figs. 1, 2, 3 and 4 gives a clue to the actual point of attack. In the case of 2,5-dimethylhexane, the oxidation does not increase with rising temperature after a total of one atom of carbon has been oxidized away as gas. In the case of 2-methyl-3-ethylpentane the reaction stops similarly when approximately two carbon atoms have been oxidized away. In the case of 3-ethylhexane, the reaction stops when three carbon atoms have been oxidized away. In the case of 3-methylheptane more than three atoms of carbon have been oxidized away at the highest temperature recorded, and the reaction is still increasing with rising temperature. Now the longest unbranched, open-end straight chain of these compounds is one, two, three and four carbon atoms in length, respectively. It seems reasonable, therefore, to interpret the reactions as follows. (I) Oxygen attacks the methyl group at the end of the longest open-end straight chain of the hydrocarbon, forming an aldehyde and water. (2) The aldehyde is oxidized with the formation of an aldehyde of one less carbon atom, water and either carbon monoxide or carbon dioxide. (3) This reaction proceeds until a branch in the hydrocarbon chain occurs, making the oxidation product a ketone instead of an aldehyde. (4) When this stage has been reached the low-temperature oxidation slows down markedly, as it would be expected that a ketone would resist further oxidation more than an aldehyde.

2,2,4-Trimethylpentane has, like 2,5-dimethylhexane, an open-end straight chain of only one carbon atom, and might be expected to behave similarly. Evidently, however, the highly condensed structure renders the hydrocarbon so resistant to oxidation that no reaction occurs at all until such high temperatures are reached that the reaction, once started, goes rapidly to completion, the high-temperature disturbance setting in at once.

(d) Low-Temperature and High-Temperature Disturbances.—As pointed out above, evidence was presented in Part I of this series that the low-temperature disturbance involves the oxidation of an aldehyde to carbon monoxide, an aldehyde of a smaller number of carbon atoms and water, the reaction being undoubtedly of the "chain reaction" type. That similar phenomena occur in the case of two out of five of the isomeric octanes is further evidence that at least in these cases a chain reaction occurs, involving the oxidation of an aldehyde. It is significant that in the three cases in which the phenomenon was not observed it is found that for 2,5-dimethylhexane and 2-methyl-3-ethylpentane less than one mole of oxygen has been consumed in this reaction, and hence it would be expected that the results of this reaction would be less apparent than in the other cases; in the case of 2,2,4-trimethylpentane, no low-temperature reaction occurs at all. In the case of 3-ethylhexane, the disturbance was only slight, and it is not surprising that it was not noticeable in the cases involving still less of the reaction in question.

The high-temperature disturbance presumably occurs when the hydrocarbon itself, or its primary oxidation products, are brought, together with oxygen, to a temperature sufficiently high for the reaction to go semi-explosively to completion. Two questions seem worthy of consideration: (a) does the reaction at the point of the high-temperature disturbance pass through the same steps as occur at lower temperatures, and (b) is some entirely new mechanism involved in the oxidation at this point? It is hardly possible to answer either of these questions definitely from the available data, but a probable answer can be given to the first one. If the oxidation proceeds always through the steps involved in the low-temperature oxidation, it would be expected that the temperature at which the high-temperature disturbance sets in would be determined (a) by the extent to which the primary oxidation has proceeded, (b) by the nature of the oxidation products and (c) by the excess oxygen present. The experimental facts seem to be in accord with this hypothesis. Thus n-octane, mixed with the theoretical quantity of air for complete combustion, does not react completely until a temperature ,of 667° has been reached, which may mean that oxygen has been consumed so readily in forming primary oxidation products that the concentration of oxygen is much reduced, and a very high temperature must be reached before the primary products can undergo semi-explosive reaction. On the other hand, in the case of 2,2,4-trimethylpentane, when oxidation begins at 515°, the concentration of oxygen is higher and the evolution of heat of the initial oxidation brings about the semi-explosive reaction at a lower temperature than is the case with n-octane. The behavior of other isomeric octanes presumably falls between these two cases, the temperature of the high-temperature disturbance depending partly on the oxygen concentration and partly on the nature of the primary oxidation products.

On the hypothesis that the reaction is the direct oxidation of the hydrocarbon, without passing through the low-temperature stage, it is most surprising that a readily oxidized hydrocarbon such as n-octane shows this reaction at a higher temperature than 2,2,4-trimethylpentane. The first hypothesis is therefore favored.

It should be realized, of course, that the actual temperatures at which these reactions occur are undoubtedly influenced by such factors as design of apparatus, oxygen concentration and oxygen–fuel ratio. The actual data given refer only to the particular conditions in question.

The reaction proceeds so rapidly at the point of the high-temperature disturbance that it is impossible to determine whether or not some new mechanism, such as "cracking," or simultaneous attack of the molecule at several points, is involved.

(e) Temperature of Initial Attack.—There is little relation between the temperature of initial attack and the other oxidation characteristics. Thus 2,5-dimethylhexane is attacked at a temperature about equal to that for n-octane, while 2,2,4-trimethylpentane is not attacked at all until very much higher temperatures have been reached. The other isomers are all attacked at slightly higher temperatures than n-octane, a slight trend being observed with increasing condensation of the molecule.

V. Probable Behavior of Other Hydrocarbons

In the first place, it should be emphasized that the conclusions reached in this paper should not be taken as indicating that oxidation of even these particular hydrocarbons must follow the course outlined above under all conditions. Many reactions of oxygen with hydrocarbons are thermodynamically possible, and the reaction under different conditions of oxygen concentration, oxygen–fuel ratio and experimental technique may doubtless follow courses quite different from those observed in this paper. It is particularly probable that the liquid-phase oxidation and the oxidation under static conditions may follow a course distinctly different from those discussed herein. The present data are perhaps of particular interest in connection with the behavior of fuels in the internal combustion engine, in that air and not pure oxygen was employed for the oxidation, and in that the dynamic method employed involves a time of contact more closely related to that of the internal combustion engine than does the static method. It is interesting to speculate on the possible behavior of hydrocarbons other than those studied. It may be reasonably expected that all normal paraffins of intermediate molecular weight will show characteristics similar to n-octane. Certain branched-chain hydrocarbons offer interesting possibilities which may be only guessed at. Thus hydrocarbons, similar to 2,5-dimethylhexane but of higher molecular weight, might conceivably be attacked toward the center of the molecule as well as the end. Highly condensed hydrocarbons such as hexamethylethane, in which the oxidation of an aldehyde could not occur in the manner noted above, might well be extremely resistant to oxidation, and hydrocarbons in which a chain is branched at a quaternary carbon atom also involve possible complications of the general scheme. It would be interesting to have data for such cases. The oxidation of olefins also is a question of much interest. A few preliminary data available in this Laboratory indicate that the oxidation of *α-n*-octene begins at a higher temperature than the oxidation of n-octane, and is otherwise analogous to the case of n-octane, which certainly suggests that the oxidation does not begin at the double bond, but at the opposite end of the hydrocarbon, and follows a course similar to that of the saturated hydrocarbons. It is to be hoped that many more data than those contained in this paper will soon be available, in order to determine many of the points which must remain for the present in doubt.

VI. Summary

1. Data have been presented on the vapor phase oxidation of five branched-chain octanes. Distinct differences exist in the behavior of these hydrocarbons toward oxygen.

2. The data have been interpreted as indicating that in general oxygen first attacks the methyl group at the end of the longest free straight chain

and that it proceeds in a manner analogous to that observed for *n*-octane (Part I) until a branch in the chain occurs, the oxidation slowing down markedly at this point.

3. Certain points of interest bearing on the general problem of hydrocarbon oxidation have been briefly discussed.

YONKERS N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE ETHYL GASOLINE CORPORATION]

THE VAPOR PHASE OXIDATION OF ISOMERIC OCTANES. III. THE EFFECT OF TETRA-ETHYL LEAD AND THE RELATION OF OXIDATION TO ENGINE DETONATION

BY J. C. POPE, F. J. DYKSTRA AND GRAHAM EDGAR

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I. Introduction

The marked effect of tetra-ethyl lead and other "anti-detonants" upon certain characteristics of the combustion of hydrocarbons in the internal combustion engine is a phenomenon which has attracted the attention of numerous investigators. In several cases the oxidation of hydrocarbons in the presence of anti-detonants has been studied, and theories have been propounded connecting the phenomena observed with the behavior of fuels in the internal combustion engine.[1] It cannot be said, however, that these theories have given a complete explanation of the effect of anti-detonants on engine detonation, and no data at all have been presented in explanation of the wide differences in engine behavior of isomeric hydrocarbons.[2] Any data bearing upon these subjects seem, therefore, to be worthy of careful scrutiny.

In Parts I and II of this paper data have been presented upon the vapor phase oxidation of six isomeric octanes and simple interpretations have been given of their behavior. In Part III there are presented data upon the oxidation of n-octane and of n-heptaldehyde in the presence of tetra-ethyl lead. The relation between the data in Parts I, II and III and the detonation tendencies of paraffin hydrocarbons in the internal combustion engine is discussed.

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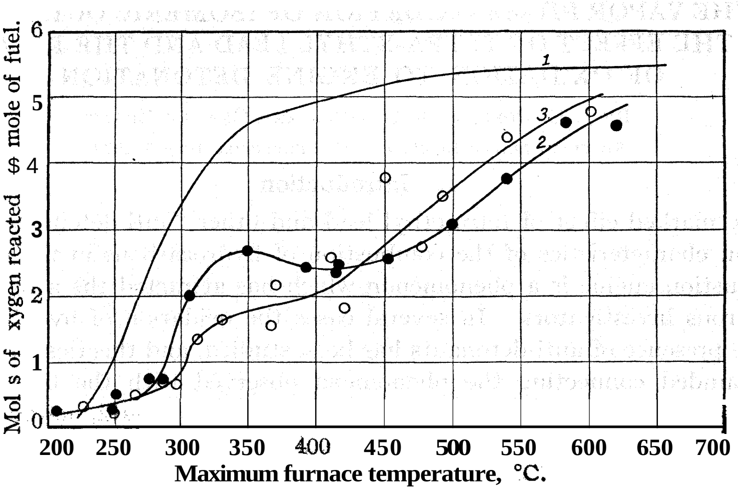
[1] (a) Callendar, Aeronautical Research Committee (London), Reports and Memoranda No. 1062 (1927); (b) Lewis, J. *Chem. Soc.*, 1555 (1927); (c) Moureu, Dufraisse and Chaux, *Compt. rend.*, 184, 413 (1927); (d) Weerman, J. *Soc. Petrol. Tech.*, 13, 300 (1927); (e) Egerton and Gates, *ibid.*, 13, 273, 281 (1927); (f) Mardles, J. *Chem. Soc.*, 872 (1928); (g) Rideal and Brunner, *ibid.*, 1162 (1928); (h) Millikan, American Petroleum Institute Bulletin, September, 1928, Project 11; (j) Layng and Youker, Ind. *Eng. Chem.*, 20, 1048 (1928); (k) Maxwell and Wheeler, *ibid.*, 20, 1041 (1928); (l) Berl, Heise and Winnacker, *Z. physik. Chem.*, 139, 453 (1928); (m) Butkov, *C. A.*, 22, 2050 (1928); 23, 966 (1929).

[2] Edgar; *Ind. Eng. Chem.*, *19*, 145 (1927).

II. Experimental Procedure

The oxidation of n-octane and of n-heptaldehyde in the presence of tetra-ethyl lead was studied in an apparatus and by a procedure identical with that employed with n-octane alone (Part I). Tetra-ethyl lead was added to the fuel and vaporized with it. Runs were carried out with slowly rising temperature and with the temperature stationary. In all cases the gaseous oxidation products were determined and in the latter case some analyses were made of the liquid oxidation products. The details of the methods of analysis, etc., were described in Part I.



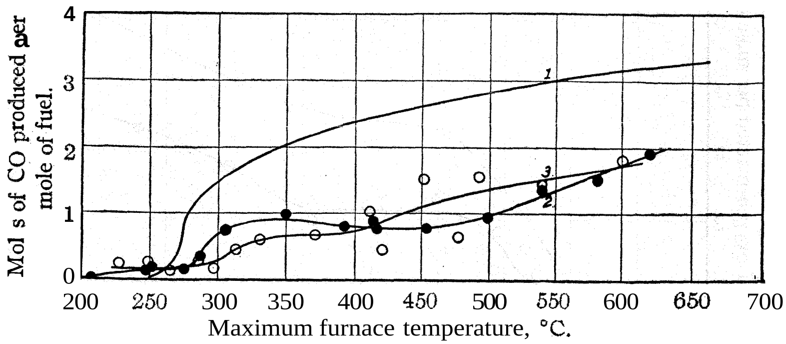
1, *n*-Octane; 2, -●-, n-octane plus 0.3% vol. lead tetra-ethyl; 3, -O-, n-octane plus 1.07% vol. of lead tetra-ethyl.

Fig. 1.—Normal octane (theoretical air/fuel ratio).

III. Experimental Data

Characteristic experimental data from rising temperature runs are expressed graphically in Figs. 1, 2 and 3 for n-octane and in Figs. 4 and 5 for n-heptaldehyde. For the sake of comparison, the corresponding data from Part I for n-octane alone and for n-heptaldehyde alone are included. The data on n-octane with tetra-ethyl lead were obtained in four individual experiments; for n-heptaldehyde the results of three experiments are included.

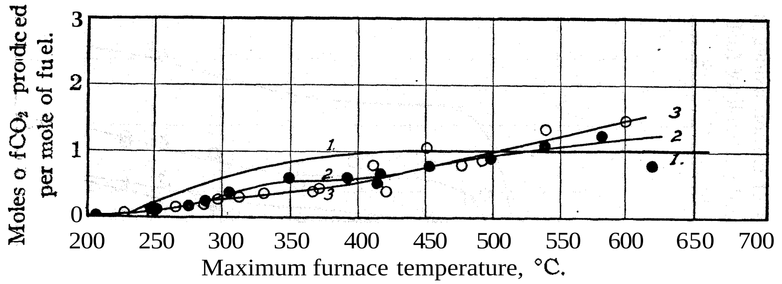
The oxygen consumption and carbon oxides produced are expressed in moles per mole of octane input and the temperatures are the maximum furnace temperature at the average time of sampling. In addition to the data in the figures it may be noted that as usual small amounts of gas absorbable in fuming sulfuric acid were found, in amounts not differing appreciably from those found in the experiments of Parts I and II. The liquid oxidation products contained aldehyde and water in considerable amounts and acid in very small amounts. The data did not differ materially from those found with n-octane in the absence of tetra-ethyl lead. The phenomena accompanying the oxidation were similar in most respects to those observed in Part I. Certain differences will be described below.



1, n-Octane; 2, –O–, n-octane plus 0.3% vol. of lead tetra-ethyl; 3, –O–, n-octane plus 1.07% vol. of lead tetra-ethyl.

Fig. 2.—Normal octane (theoretical air/fuel ratio).

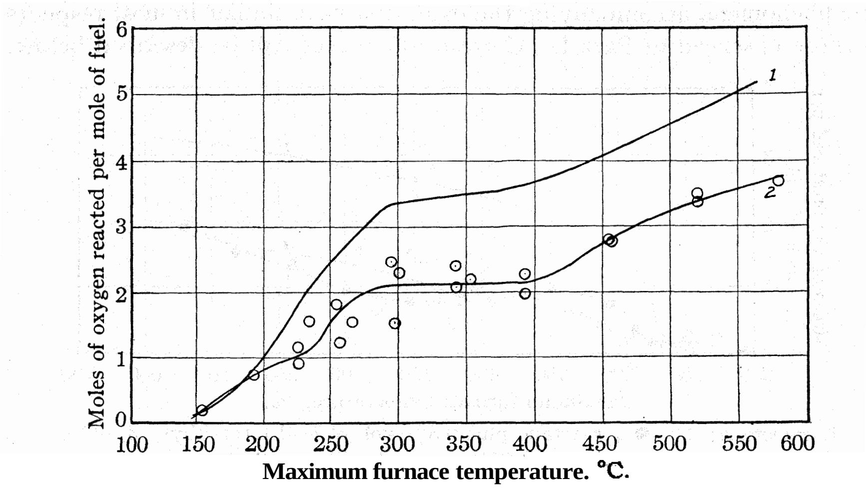
It may be noted that the experimental data in the presence of rather large amounts of tetra-ethyl lead were much more erratic than those observed with the hydrocarbons alone. This is not altogether unexpected, since under the conditions of the experiments tetra-ethyl lead undergoes oxidation, in amount varying with the temperature. The extent of such oxidation, the point at which it occurs in the furnace and the distribution of the products through the furnace undoubtedly vary with the temperature and perhaps between runs, and may account for the somewhat erratic results. The varying effect of tetra-ethyl lead at different temperatures, discussed below, may also be at least partially due to the decomposition phenomena. For the purpose of this paper no distinction is made between tetra-ethyl lead itself and its various decomposition products, as the data



1, n-Octane; 2, —O—, *n*-octane plus 0.3 % vol. of lead tetra-ethyl; 3, —O—, n-octane plus 1.07% vol. of lead tetra-ethyl.

Fig. 3.—Normal octane (theoretical air/fuel ratio).

herein presented do not permit an analysis close enough to determine such distinctions, if they exist.

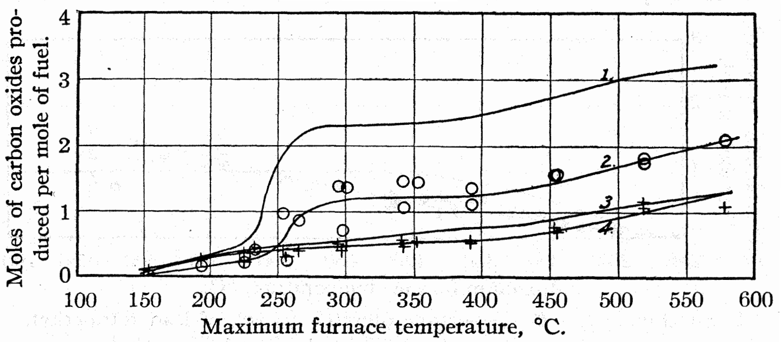


1, n-Heptaldehyde; 2, –O–, *n*-heptaldehyde plus 1% vol. of lead tetra-ethyl.

Fig. 4.—Normal heptaldehyde (theoretical air/fuel ratio).

IV. Discussion of Data

Comparison with the Data in the Absence of Tetra-ethyl Lead.—In Fig. 1 a comparison is made of the oxygen consumption of n-octane at different temperatures with and without tetra-ethyl lead. In Fig. 2 a similar comparison is made of the carbon monoxide produced and in Fig. 3 of the carbon dioxide produced. In Fig. 4 the oxygen consumption data for heptaldehyde with and without tetra-ethyl lead are compared, and in



n-Heptaldehyde: 1, CO produced; 3, CO_2 produced.
n-Heptaldehyde plus 1% vol. lead tetra-ethyl: 2, –O–, CO produced; 4, – + –, CO_2 produced.

Fig. 5.—Normal heptaldehyde (theoretical air/fuel ratio).

Fig. 5 the carbon oxides formed are compared. An analysis of these data follows.

(1) ***n*-Heptaldehyde.**—Data were presented in Part I indicating that aldehydes are intermediate oxidation products of n-octane, and that the carbon oxides formed are the oxidation products of such aldehydes, rather than of n-octane directly. In attempting to determine the exact effect of tetra-ethyl lead it seems therefore desirable to consider first the oxidation of n-heptaldehyde in the presence of tetra-ethyl lead, since in this case only two of the three reactions involved in the oxidation of n-octane are concerned. It is clear from the data in Figs. 4 and 5 that practically the entire effect of tetra-ethyl lead on the oxidation of n-heptaldehyde is upon the reaction producing carbon monoxide. The carbon dioxide formed with tetra-ethyl lead differs from that formed in its absence by little more than the experimental error. The carbon monoxide is, however, greatly reduced in the presence of tetra-ethyl lead, and the data for oxygen consumption differ from those without tetra-ethyl lead by an amount corresponding almost exactly to the reduction in carbon monoxide, since one mole of oxygen is consumed in the production of one mole of carbon monoxide. It would be expected that the reaction involving carbon monoxide would be the one most apt to be affected by tetra-ethyl lead, since it is a "chain" reaction (Part I), and such reactions are usually capable of marked retardation by negative catalysts. Presumably the reaction is normally propagated through the medium of a reaction chain in which "activated molecules" in reacting activate other molecules. Tetra-ethyl lead probably retards the reaction by accepting the surplus energy of such molecules and thus breaking the reaction chain.

The temperature at which the "low temperature disturbance" begins with its accompanying luminescence and pulsations, is distinctly raised by tetra-ethyl lead, (235 to 270°), as would be expected from the fact that the reaction producing this disturbance is suppressed. The range over which the disturbance is noticeable is, however, not measurably affected. It may be noted that at very low temperatures tetra-ethyl lead has very little if any effect upon the oxidation of heptaldehyde, a phenomenon perhaps associated with the fact that tetra-ethyl lead is not decomposed appreciably under the conditions of the experiment in this temperature range. The effect also is diminished at quite high temperatures, which may again be associated with the decomposition phenomena.

(2) n-Octane.+-Octane, according to the view expressed earlier by the authors, differs in its essential oxidation mechanism from n-heptaldehyde only by the initial reaction in which aldehyde is produced from the hydrocarbon. The data in Figs. 1, 2 and 3 are fully in accord with this view. Thus the most striking effect of tetra-ethyl lead is in the suppression of the reaction in which carbon monoxide is formed, a suppression which would be expected from the data on n-heptaldehyde. There is evidence, however, of another effect of tetra-ethyl lead. Thus while oxidation begins at about the same temperature in the presence of tetra-ethyl lead as in its absence, the oxygen consumption rises with increasing temperature somewhat more slowly than can be accounted for by the suppression of the carbon monoxide alone, particularly at low and intermediate temperatures. This suggests that the primary oxidation of n-octane to aldehyde is somewhat retarded and that complete oxidation of the hydrocarbon does not occur in the presence of tetra-ethyl lead until a higher temperature has been reached than is necessary with n-octane alone. The data on carbon dioxide production support this view, since they are slightly lower, at low temperatures, in the presence of tetra-ethyl lead than in its absence, as would be expected if the formation of aldehyde (from which the carbon dioxide is produced) is somewhat retarded. The apparent partial reduction in the primary oxidation of *n*-octane suggests the possibility that this reaction may also be of the chain reaction type, but no further evidence is available.

The effect of tetra-ethyl lead on the low temperature disturbance with n-octane is similar to its effect upon the corresponding disturbance in the case of n-heptaldehyde, in that the temperature at which the disturbance begins is raised (270 to 300°), but with n-octane the disturbance is much less vigorous in the presence of tetra-ethyl lead than in its absence, the luminescent flashes are more frequent and the temperature range over which the disturbance lasts is increased. This seems in accord with the hypothesis that the primary oxidation of n-octane is partially suppressed and the aldehyde oxidation (to carbon monoxide) strongly suppressed. Other facts worth recording in connection with the oxidation are: (1) that, as with *n*-heptaldehyde, the effect of tetra-ethyl lead seems to decrease at high temperatures; (2) that the data were not extended to the temperature of the "high temperature disturbance," so that it cannot be determined whether or not this point is affected by tetra-ethyl lead; and (3) that increasing the concentration of tetra-ethyl lead from 0.31 vol. per cent. to 1.00 vol. per cent. does not produce a corresponding effect on the oxidation phenomena.

V. Relation of Oxidation Phenomena to Engine Detonation

The facts that tetra-ethyl lead effectively suppresses detonation in the internal combustion engine, and that its chief effect upon the oxidation of a hydrocarbon having a high tendency to detonate (n-octane) is the suppression of certain oxidation reactions, suggest a close relationship between the two phenomena. It is interesting in this connection to examine the behavior in the engine of the isomeric octanes whose oxidation characteristics were discussed in Part II. Insufficient amounts of these hydrocarbons were available to enable their tendencies to detonate to be measured on the pure materials; accordingly, they were dissolved in gasoline in the proportion of 10% by volume, and their effect on the tendency of the gasoline to detonate was measured in an engine, employing a technique previously described.[3] The hydrocarbons arranged themselves in the following order, the one having the greatest tendency to detonate being given first: (1) n-octane, (2) 3-methylheptane, (3) 3-ethylhexane, (4) 2-methyl-3-ethylpentane, (5) 2,5-dimethylhexane and (6) 2,2,4-trimethylpentane. Now it has been previously shown (Part II) that the first five of these hydrocarbons have their longest open-end straight chains of eight, four, three, two and one carbon atoms, respectively, and that the length of these chains determines the extent to which the low temperature oxidation can proceed. The sixth hydrocarbon (2,2,4-trimethylpentane) was found to be entirely unoxidized at low temperatures.

We have here, therefore, a striking correlation between engine detonation and oxidation characteristics. This may be recapitulated as follows. (1) A "chain reaction" involving the oxidation of an aldehyde to carbon monoxide, water and another aldehyde has been found to be one of the chief oxidation reactions of the five isomeric hydrocarbons which undergo appreciable oxidation at low temperatures. (2) The extent to which this reaction is capable of proceeding without interruption is determined by the length of the longest open-end straight chain of carbon atoms in the mole-

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[3] Edgar, J. Soc. *Automotive* Eng., **22,** 41 (1928).

cule, and the oxidation actually slows down when it has proceeded to a point corresponding to the length of such a chain (unless a secondary disturbance sets in before such point is reached). (3) Tetra-ethyl lead sharply retards this reaction (in the one case studied), and apparently reduces somewhat the primary oxidation of the hydrocarbon. (4) The tendency of these hydrocarbons to detonate follows the same order as that of the extent to which this reaction occurs at low temperatures, and the hydrocarbon showing no low temperature oxidation has less tendency to detonate than any of the others. (5) Tetra-ethyl lead reduces the tendency of a fuel to detonate.

Apparently, therefore, both the temperature of initial oxidation and the extent to which such oxidation proceeds are factors involved in the detonation phenomena. If the relationships found for the six octanes are general, it seems reasonable to predict that as far as the paraffin hydrocarbons are concerned: (a) for normal hydrocarbons the tendency to detonate will increase with increasing molecular weight (this is known to be in accord with experiment); (b) branched-chain hydrocarbons which undergo oxidation at low temperatures will have a tendency to detonate increasing with the length of the longest open-end carbon chain; (c) hydrocarbons resistant to low temperature oxidation will have little tendency to detonate (*e.g.*, 2,2,4-trimethylpentane). These will probably have highly condensed structures. It must be admitted that the data on which these conclusions are based are not as complete as could be wished, but they appear to give quite clear indications of the phenomena to be expected with different paraffin hydrocarbons.

VI. Mechanism of Detonation

It is much more difficult to suggest a satisfactory mechanism of engine detonation. So many factors involved in the combustion of fuels in an engine are widely different from those in the laboratory experiments that too close an analogy can hardly be expected. We know little concerning the chemical changes involved in the combustion of fuel in an engine except that Lovell, Coleman and Boyd[4] have shown that the combustion is more rapid when an engine is detonating than during normal operation. In an engine the air–fuel mixture is first compressed to about five atmospheres in a hot cylinder. It is then ignited with a spark and the mixture burns either with or without the development of detonation. It is probable that temperatures of 400–500° are reached during the compression stroke before the spark is fired. It is quite conceivable that when readily oxidized hydrocarbons are used as fuel appreciable oxidation may occur during the compression stroke, and that the rate of burn of the mixture after the charge is fired (and the tendency to detonate) may depend upon the extent of such

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[4] Lovell, Coleman and Boyd, *Ind. Eng. Chem.*, **19**, 373 (1927).

preliminary oxidation. It is also possible that the rate of burn of a charge fired by a spark may depend upon factors similar to those which govern the low temperature oxidation. The problem is extremely complicated and the authors do not feel that the data presented in this paper give by any means the complete account of engine detonation. Nevertheless, they represent an interesting correlation of laboratory data with engine operation, and are presented with the hope that they may contribute to clearing up at least certain phases of this important problem.

VII. Summary

1. Experimental data have been presented on the vapor phase oxidation of n-octane and n-heptaldehyde in the presence of tetra-ethyl lead.
2. The effect of tetra-ethyl lead seems to be chiefly that of slowing down the oxidation of aldehydes to carbon monoxide, water and other aldehydes.
3. The data, combined with those of Parts I and II, are discussed in comparison with the behavior of the hydrocarbons as fuel in the internal combustion engine, and certain correlations are pointed out.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

THE ACTION OF PHENYL ISOCYANATE ON URETHANS, UREAS AND THIOUREAS

BY HANS LAKRA[1] AND F. B. DAINS

RECEIVED MARCH 22, 1929 PUBLISHED JULY 5, 1929

Phenyl isocyanate, which was first obtained by A. W. Hofmann,[2] is characterized by its ability to form addition products with the N=C double bonding. Thus with alcohols urethans, $C_6H_5NHCOOR$, are formed while with ammonia and with primary and secondary amines, substituted ureas result. The presence of aryl groups in the secondary amines often tends to slow up or even in some cases to prevent the expected addition, $RR'NH + C_6H_5NCO = C_6H_5NHCONRR'$.

Since the nature of the hydrocarbon (aryl) group has been found to affect the course of the reaction, it seemed worth while to study the reactivity of phenyl isocyanate toward the group $RNH(NH_2)$ when it was linked with a CO or CS complex, in order to determine their influence upon the expected additions.

In the present investigation the compounds chosen were urethans, ureas and thioureas where the primary reaction might be expected to yield (a)

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[1] From a dissertation presented by Hans Lakra to the Faculty of the Graduate School of the University of Kansas, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Hofmann, Ann., 74, 9 (1850); *Ber.*, 3, 655 (1870).

with urethans, allophanic esters, $C_6H_5NHCONHCOOR$; with ureas, biurets, $C_6H_5NHCONHCONH_2$, and with thioureas, monothiobiurets, $C_6H_5NHCONHCSNH_2$, or their substitution products where an H had been replaced by aryl or alkyl groups.

Such addition products were isolated in a number of cases; in others only the dissociation products of the initial compound. Any simple formulation of the results was rendered difficult in many instances by the fact that one of the dissociation products was isocyanic acid, which could then condense with itself to form isocyanuric acid or with amino compounds, yielding ureas or biurets. Higher temperatures favored this latter type of reaction.[3]

Experimental

Phenyl Isocyanate and **Urethan.**—Molecular proportions of the two reagents were heated at 140–160° for six hours.[4] From the reaction product were isolated: (1) phenyl allophanic ester, $C_6H_5NHCONHCOOC_2H_5$; (2) phenylurethan, $C_6H_5NHCOOC_2H_5$; (3) phenylisocyanuric acid, $C_6H_5H_2C_3O_3N_3$; and (4) phenylcarbethoxybiuret, $C_6H_5NHCONHCONHCOOC_2H_5$. No. 1 is formed by direct addition; Nos. 2 and 3 by dissociation of the urethan into HNCO and alcohol and subsequent addition of alcohol or the dimer $(HNCO)_2$ to the isocyanate, while in No. 4 the phenylisocyanate and alcohol add to $(HNCO)_2$. No evidence was obtained as to the intermediate possible formation of allophanic ester which with the isocyanate would yield the carbethoxybiuret.

Phenyl Isocyanate and **Phenylurethan.**—Heated at 150° a little carbanilide is formed.[5] At temperatures from 200–250° this is the main product. While the phenylurethan would account for part of the carbanilide, the increased amount would indicate that the ethyl alcohol from the urethan loses a mole of water which then reacts with additional isocyanate to form diphenylurea.[6]

Phenyl Isocyanate and **Ethylurethan,** $C_2H_5NHCOOC_2H_5$.—The mixture was heated at 175° for six hours. The only product isolated was diphenylurea. No ethylphenylurea or diethylurea was detected due to the volatility of the dissociation products, ethylamine and ethyl isocyanate.

Phenyl Isocyanate and **Allophanic** Ester.—The two compounds failed to react at 125°. At 160° unchanged allophanic ester, carbanilide and isocyanuric acid were isolated.

Anal. Calcd. for $C_3H_3N_3O_3$: N, 32.55. Found: N, 32.13.

Heated at 170–178° an additional product, phenylisocyanuric acid was obtained.

Anal. Calcd. for $C_9H_7N_3O_3$: N, 20.48. Found: N, 20.10.

Allophanic ester alone slowly decomposes at 160°, yielding ammonia and isocyanuric acid. The carbanilide is due to the intermediate formation of phenylurea ($C_6H_5NCO + NH_3$) and the phenylisocyanuric acid is formed as indicated in the case of urethan.

Phenyl Isocyanate and Urea.—After heating at water-bath temperature for seven hours, there was isolated a little diphenylurea, and unchanged urea, but the main

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[3] This work harmonizes with the results on "Urea Dearrangement," Davis and Underwood, THIS JOURNAL, 44, 2595 (1922); Davis and Blanchard, *ibid.*, **45,** 1816 (1923).

[4] Dains, Greider and Kidwell, *ibid.*, **41,** 1008 (1919).

[5] Schiff, *Ber.*, **3,** 249 (1870).

[6] Dains, THIS JOURNAL, 21, 180 (1899).

product was α-monophenylbiuret, $C_6H_5NHCONHCONH_2$, formed by simple addition. This, after recrystallization from hot water and from dilute alcohol, melted at 156–157°.[7]

Anal. Calcd. for $C_8H_9N_3O_2$: N, 23.48. Found: N, 23.60, 23.27.

Phenyl Isocyanate and Urea at **120°** for Four Hours.—In this case the following products were isolated and identified: ammonia, unchanged urea, **biuret,**[8] diphenylurea, monophenylurea, phenylisocyanuric acid[B] and isocyanuric acid.

The results are in harmony with what might be predicted from a mixture containing phenyl isocyanate, urea, ammonia and isocyanicacid ($NH_2CONH_2 \rightleftarrows NH_3 + HNCO$).

$$2C_6H_5NCO + 2NH_3 = 2C_6H_5NHCONH_2 = (C_6H_5NH)_2CO + NH_2CONH_2$$
$$NH_2CONH_2 + HNCO = NH(CONH_2)_2$$
$$3HNCO = C_3H_3N_3O_3$$
$$C_6H_5NCO + 2HNCO = C_6H_5H_2C_3N_3O_3$$

Results When Heated at **140°** for Seven Hours.—The main product was carbanilide. No biuret or monophenylurea was isolated.

Acyl Substituted **Ureas.**—Phenyl isocyanate and acetylurea failed to react at water-bath temperature, but heated at 130 or 160° for five hours, the same products were obtained, *viz.,* α-acetyl-β-phenylurea and isocyanuric acid. The results could be due either to the action of the isocyanate upon acetamide, ($CH_3CONHCONH_2 \rightleftarrows CH_3CONH_2 + HNCO$), or addition to the acetylurea, as follows: $CH_3CON(CONHC_6H_5)CONH_2$ and then loss of HNCO.

The fact that no phenylisocyanuric acid was detected is in favor of this latter formulation.

In the same way benzoylurea and the isocyanate yielded at 150° benzoylphenylurea, which at 210° slowly dissociated into phenylisocyanate and benzamide (m. p. 128").

Phenyl Isocyanate and **Monophenylurea.**—Kuhn and Henschel digested the above mixture[10] at 120° and reported the formation of 1,5-diphenylbiuret and traces of a higher-melting product. On repeating their work but only heating at 100° for four hours, there was obtained diphenylurea, 1,5-diphenylbiuret,[11] m. p. 210°, and monophenylbiuret, m. p. 156–157°, confirmed by a mixed melting point with a known sample of monophenylbiuret.

The result would seem to indicate that the isocyanate can add to the phenylurea at two points; first at Position 3, yielding the 1,5-diphenylbiuret, and at Position 1, giving the isomeric biuret, $C_6H_5NHCON(C_6H_5)CONH_2$. This dissociates into diphenylurea and isocyanic acid, which then adds to the unchanged phenylurea. The same products would be formed if it were assumed that some of the phenylurea dissociated, $C_6H_5NHCONH_2 = C_6H_5NH_2 + HNCO$, but this seems a question at 100°.

The fact that phenylurea when boiled for several hours with water yields aniline can well be regarded as a simple case of hydrolysis.[12]

Disubstituted **Ureas.**—Carbanilide and phenyl isocyanate at 150° gave 1,3,5-triphenylbiuret (m. p. 147°).[13] Above its melting point the biuret is unstable, breaking down into carbanilide and the isocyanate.

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[7] Piccard and Carter, *J. Chem. Soc.,* **79,** 846 (1900); **81,** 1563 (1902); McKee, *Am. Chem. J.,* **26,** 254 (1901); Dains and Wertheim, THIS JOURNAL, **42,** 2307 (1920); Gatewood, *ibid.,* **47,** 407 (1925).

[8] *Anal.* Calcd. for $C_2H_5N_3O_2$: N, 40.79. Found: N, 40.53, 40.46.

[9] *Anal.* Calcd. for $C_9H_7N_3O_3$: N, 20.48. Found: N, 20.23.

[10] Kuhn and Henschel, *Ber.,* **21,** 504 (1888).

[11] *Anal.* Calcd. for $C_{14}H_{13}N_3O_2$: N, 16.47. Found: N, 16.34.

[12] Davis and Blanchard, THIS JOURNAL, **45,** 1818 (1923).

[13] Hofmann, *Ber.,* 4,250 (1871); Kuhn and Henschel, *Ber.,* **21,** 504 (1888).

Anal. Calcd. for $C_{20}H_{17}N_3O_2$: N, 12.68. Found: N, 16.34.

Methylphenylurea and phenyl isocyanate failed to react at 100° but at 135–140° carbanilide alone was obtained, the probable intermediate 1,3-diphenyl-5-methylbiuret not being stable at this temperature.

Phenylacetylurea does not combine with the isocyanate at 150°, but at 200° diphenylurea is the main product. The acetylurea dissociates at this temperature into phenylisocyanate and acetamide; loss of a mole of water converts the isocyanate into diphenylurea.

Phenyl Isocyanate and Thiourea

1-Phenyl-4-thiobiuret, $C_6H_5NHCONHCSNH_2$.—This was formed in good yield when the two substances were heated at water-bath temperature for five hours. The residue was washed with dry ether and recrystallized from alcohol. It then melted at 186°.

Anal. Calcd. for $C_8H_9N_3OS$: N, 21.55. Found: N, 21.78, 21.67.

Its constitution was proved by the fact that on desulfurization with lead hydroxide in alcohol solution, α-monophenylbiuret was obtained. At 110" the thiourea and isocyanate yielded the same biuret mixed with carbanilide, the amount of which increased with rising temperature.

1-Phenyl-4-methylthiobiuret, $C_6H_5NHCONHC(CH_3){=}NH$.—When the thiobiuret was heated with methyl iodide in a sealed tube in the water-bath, the hydrogen iodide salt was formed. Alkali precipitated from its water solution the free base, which when crystallized from alcohol melted at 147–8°.

Anal. Calcd. for $C_9H_{11}N_3OS$: N, 20.10. Pound: N, 20.00, 20.19.

Mono- and Di-substituted **Thioureas.**—In no case was it possible to isolate addition products from the mono- and disubstituted thioureas. The sole products identified were diphenylurea and mustard oils. Thus allylthiourea and phenylthiourea reacted slowly at water-bath temperature, completely at 110–120°, yielding carbanilide and allyl- or phenylisothiocyanate, while allylphenylthiourea or diphenylthiourea at 120–130° gave quantitatively diphenylurea and allyl- or phenylisothiocyanate.[14]

Addition of Phenyl Isocyanate to the Isothiourea Ethers

Methylthiocarbonyldiphenyldiurea, $C_6H_5NHCON{=}C(SCH_3)NHCONHC_6H_5$.—The methyl iodide addition product of thiourea (22 g.) was dissolved in as little water as possible. To this was added phenyl isocyanate (24 g.) and a concentrated solution of potassium hydroxide (5–6 g.). On shaking a viscous mass was formed which slowly solidified. Purified from alcohol, it melted at 142°.

Anal. Calcd. for $C_{16}H_{16}N_4O_2S$: N, 17.07. Found: N, 16.82, 16.78. Mol. *wt.* in acetic acid: calcd., 328. Found: 289.

The same compound (m. p. 142") was obtained from 1-phenyl-4-methylthiobiuret and the isocyanate.

The thio-ether was warmed for a few minutes with one mole of alcoholic potassium hydroxide, hoping thus to obtain the carbonyldiphenyldiurea. Instead the ether broke down into mercaptan, aniline and a product soluble in alkali which proved to be phenylisocyanuric acid.

Anal. Calcd. for $C_9H_7N_3O_3$: N, 20.48. Found: N, 20.19.

When the thio-ether was treated with potassium sulfhydrate, mercaptan was

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[14] Goldschmidt and Meissler, Ber., 23,273 (1890).

eliminated with the formation of thiocarbonyldiphenyldiurea, $CS(NHCONHC_6H_5)_2$; m. p. 202°.[15]

The Ethyl Ether of Thiocarbonyldiphenyl-diurea, $C_6H_5NHCONHC(SC_2H_5){=}NCONHC_6H_5$.—This was prepared from γ-ethylthiourea and phenyl isocyanate. Crystallized from 50% alcohol it melted at 145°.

Anal. Calcd. for $C_{17}H_{16}N_4O_2S$: N, 16.37. Found: N, 16.87.

Phenyl Isocyanate and the Methyl Ether of **Phenylthiourea.**—The two compounds united with the development of heat and gave 1,5-diphenyl-4-methylthiobiuret, $C_6H_5NHCON{=}C(SCH_3)NHC_6H_5$, melting at 108°.

Anal. Calcd. for $C_{15}H_{15}N_3OS$: N, 14.73. Found: N, 14.94.

The methyl thio-ether when treated with KSH yielded the corresponding 1,5-diphenyl-mono-thiobiuret, $C_6H_5NHCONHCSNHC_6H_5$, melting at 161°.

As shown by Johnson[16] and confirmed by our work, γ-methylthiourea combined with only one mole of phenyl mustard oil, yielding 1-phenyl-2-thio-4-methylthiobiuret (m. p. 122").

These thio-ethers exhibit an interesting analogy to the corresponding oxygen isourea ethers in that both types add one mole of phenyl isothiocyanate and two moles of the phenyl isocyanate."

Phenyl Isocyanate and the Ethyl Ether of Diphenylthiourea, $C_6H_5NHC(SC_2H_5)NC_6H_5$.—While no action was observed at 100°, two varying sets of results were obtained at higher temperatures. Thus the isocyanate (24 g.) and the thio-ether (52 g.) heated at 160–170° for three hours gave diphenylurea, phenyl mustard oil and triphenylcyanuric acid (m. p. 270°). Evidently in this case a portion of the isocyanate had condensed to the cyanuric acid and it is possible that the expected addition product, $C_6H_5NHCONC_6H_5C(SC_2H_5)NC_6H_5$, has broken down into carbanilide, phenyl mustard oil and ethylene, although this latter was not identified.

After heating in a sealed tube at 200°, the tube opened with pressure and the issuing gases had the odor of mercaptan. The reaction product consisted of diphenylurea and a thick oil soluble in ether which after distillation in a vacuum and crystallization from alcohol melted at 162°. It gave no test for sulfur and gave figures on analysis corresponding to carbodiphenylimide, $(C_6H_5N)_2C$.

Anal. Calcd. for $C_{13}H_{10}N_2$: N, 14.43. Found: N, 14.28.

No mustard oil or triphenylcyanuric acid was found. Evidently at 200° much of the thio-ether dissociated directly into mercaptan and carbodi-imide, a reaction which has been previously observed.

Guanidine Carbonate and Phenyl Isocyanate

The Diphenylamide of Guanidine Dicarboxylic Acid, $HN{=}C(NHCONHC_6H_5)_2$.—Michael[18] had obtained this compound by the action of the isocyanate on the guanidine carbonate and sodium ethylate. It was found that potassium hydroxide could be used with good results instead of the ethylate in concd. water solution. It melted at 174°.

Anal. Calcd. for $C_{15}H_{15}N_5O_2$: N, 23.57. Found: N, 23.82.

Action on Hydrolysis.—The diamide when refluxed for thirty minutes with 15% isodium hydroxide solution gave ammonia, aniline, diphenylurea and isocyanuric acid.

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[15] Unpublished investigation by John F. Olin, who has found that KSH hydrolyzes isothiourea ethers to the corresponding thio carbonylcompounds.

[16] Johnson, *Am. Chem.* J., 29, 482, 490 (1903); 30, 172 (1903).

[17] McKee, *Am. Chem.* J., 26, 233 (1901); Bruce, THIS JOURNAL, 26, 448 (1903).

[18] Michael, J. *prakt. Chem.*, [2] *49*, 42 (1904).

Anal. Calcd. for $C_3H_3N_3O_3$: N, 32.56. Found: N, 32.40.

When heated alone at 190–200° for three hours, ammonia, diphenylurea and isocyanuric acid were identified as decomposition products.

The observation was confirmed that guanidine unites with only one mole of phenyl isothiocyanate.[19] Its behavior in this respect is analogous to the isourea and isothiourea ethers.

Summary

1. Direct addition products of phenyl isocyanate were obtained with the following: urethan, urea, mono- and diphenylurea, thiourea and all isothiourea ethers containing a free NH grouping.

2. In all other cases, the results obtained were due (a) either to addition and subsequent breaking down of the addition product or (b) dissociation at the elevated temperature of the urethan, urea, etc., as

$$C_6H_5NHCONH_2 \rightleftharpoons C_6H_5NCO + NH_3 \rightleftharpoons C_6H_5NH_2 + HNCO$$
$$NH_2CONH_2 \rightleftharpoons NH_3 + HNCO$$
$$C_6H_5NHCOOC_2H_5 \rightleftharpoons C_6H_5NCO + HOC_2H_5$$

and the re-uniting of phenyl isocyanate and these fission products in various ways. This is illustrated especially by the formation of isocyanuric acid and its derivatives.

3. Thiourea ethers, isothiourea ethers and guanidine unite with **two** moles of phenyl isocyanate but with only one mole of phenyl isothiocyanate.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XIX. IMPROVEMENTS IN THE PREPARATION OF ALDONIC ACIDS[1]

BY C. S. HUDSON AND H. S. ISBELL

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Introduction

It is customary to prepare an aldonic acid by the oxidation of the corresponding aldose with bromine water. The reaction is a slow one because of the retarding influence of the hydrobromic acid that is produced during its course.[2] If the aldose is not a monosaccharide it may be partly hydrolyzed by the hydrobromic acid, with a resulting poor yield of the desired acid. Thus Fischer and Meyer's[3] oxidations of lactose and maltose to their

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[19] Bamberger, Ber., 13, 1581 (1880).

[1] Publication approved by the Director of the Bureau of Standards. No. XVIII, Phelps and Hudson, THIS JOURNAL, 50, 2049 (1928).

[2] Bunzel and Mathews, THIS JOURNAL, 31, 464 (1909); Bunzel, *J. Biol. Chem.*, 7, 157 (1910).

[3] Fischer and Meyer, Ber., 22, 361, 1941 (1889).

respective aldobionic acids by bromine water gave yields of only about 30% and Kunz and Hudson[4] obtained similar yields in oxidizing neolactose. In these cases the isolation of the aldobionic acid was rendered difficult by the presence of gluconic and galactonic acids resulting from hydrolysis. Recently Goebel[5] has used the iodine oxidation in alkaline solution to produce aldobionic acids in nearly quantitative yield. The method obviously avoids any hydrolysis by acids and should be very suitable in researches where small quantities of sugars are to be oxidized. In larger scale preparations,[6] however, the cost of the iodine and barium iodide becomes important and for this reason we have sought to modify the plan of the bromine oxidation with the aim of making it a nearly quantitative reaction suitable for large-scale preparations. The modification which has brought success is a simple one, namely, the addition of a salt of a weak acid to the sugar solution. This acts as a buffer and keeps the hydrogen-ion concentration at a low acidity because the hydrobromic acid is neutralized by the salt and is replaced by the weak acid. The maintaining of the acidity of the solution at a low value results in the reduction of the acid hydrolysis of compound sugars to a negligible amount, and in an important increase in the speed of the oxidation. The choice of a suitable buffering salt was made on the basis that its acid and basic constituents would not interfere with the isolation of the aldonic acid. The benzoates of barium and calcium have met these requirements very well. The details of the recommended procedure will be shown by the following examples of typical preparations.

Preparation of Calcium **Gluconate.**—Six cc. of bromine (0.12 mole) was added to an ice-cold solution of 18 g. (0.1 mole) of anhydrous glucose and 60 g. (0.15 mole) of barium benzoate in 750 cc. of water. The bromine rapidly dissolved when the solution was shaken and crystals of benzoic acid soon formed. Although a faint but definite Fehling's test for reducing substances was obtained when light was not excluded, a Fehling's test of the mixture after it had stood for thirty-six hours at room temperature (20–25°) in darkness was negative, indicating the oxidation of all of the sugar. The excess bromine was removed by a stream of air and the barium was precipitated quantitatively with sulfuric acid, about 60 cc. of 5 N H_2SO_4 being required. The barium sulfate was filtered off by suction, after the addition of about 10 g. of active carbon. The hydrobromic acid was removed quantitatively by the use of lead carbonate (27 g.) followed by silver benzoate (5 g.). A more rapid removal is obtained if silver carbonate (28 g.) is used in place of lead carbonate. Soluble silver and lead salts were then removed as sulfides and the filtrate was concentrated to 200 cc. under reduced pressure. The slight quantity of dissolved benzoic acid was largely removed by several extractions

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[4] Kunz and Hudson, THIS JOURNAL, 48, 2435 (1926).

[5] Goebel, *J. Biol.* Chem., 72, 801 (1927).

[6] Stoll and Kussmal, U. S. Patent 1,648,368, Nov. 8, 1927, describe a method for the preparation of aldonic acids in good yields from the corresponding sugars by chlorine oxidation in the presence of a bromide or iodide. The method is excellent for the commercial preparation of the acids but the conditions must be carefully controlled; consequently the method is not particularly desirable for general laboratory preparations.

with chloroform. The resulting aqueous solution of gluconic acid was colorless and did not reduce Fehling's solution. It was neutralized with calcium carbonate and concentrated to about 75 cc. The addition of ten volumes of 95% alcohol precipitated granular calcium gluconate, which weighed 21.5 g. after drying at 80°. The crude product was recrystallized by solution in 100 cc. of boiling water, addition of 2 g. of active carbon, filtration, concentration of the filtrate to 50 cc. and the addition of a small quantity of alcohol. After standing overnight in an ice box the crystals were separated, washed with 50% alcohol and dried; yield, 20.2 g. The mother liquor yielded only 0.25 g. The total yield of the recrystallized product was thus 96% of the theoretical. The specific rotation of the calcium gluconate in about 3% aqueous solution was $[\alpha]_D^{20} = +8.5$.

Preparation of the Cadmium Xylonate–Cadmium Bromide Double **Salt.**[7]—Six cc. of bromine (0.12 mole) was added to an ice-cold solution of 15 g. of d-xylose (0.1 mole) and 60 g. of barium benzoate in 1500 cc. of water and the oxidation conducted in the dark at 20–25°. The solution gave a negative Fehling test after thirty-six hours. The excess bromine and the barium were removed as described for the gluconate preparation and the dissolved benzoic acid was extracted with chloroform. The solution was then boiled with 28.5 g. of cadmium carbonate to neutral reaction, filtered and concentrated to a thin sirup under reduced pressure. Addition of a little alcohol and crystallization overnight in the ice box yielded 29.1 g. of the double salt, after washing with alcohol and drying at 80°. The mother liquor yielded 3 2 g. of crystals and the total yield was 90% of the theoretical. The specific rotation of the double salt in 1.5% aqueous solution was $[\alpha]_D^{20} = +8.8$. The only previous record seems to be that by C. A. Browne,[8] who found +7.4.

Preparation of Calcium **Lactobionate.**—Six cc. of bromine (0.12 mole) was added to an ice-cold solution of 36 g. of a-lactose monohydrate (0.1 mole) and 60 g. of barium benzoate (0.15 mole) in 1500 cc. of water and the oxidation conducted in the dark at 20–25°. The solution gave a negative Fehling test in from thirty-six to forty-eight hours. Free bromine and barium were removed as described for the gluconatc preparation and the hydrobromic acid was removed by stirring the solution with lead carbonate (27 g.), filtering off the lead bromide and removing the last traces of dissolved bromide with silver benzoate (5 g.).[9] The filtrate then showed no reaction with silver nitrate. Lead and silver were then removed as sulfides and benzoic acid was largely removed by several extractions with chloroform, finally blowing out the dissolved chloroform with air. The resulting solution contains no sugar by the Fehling test, is colorless and represents a nearly pure solution of lactobionic acid.

The substance may be further purified through its basic calcium salt. The addition of 37 g. of calcium hydroxide to the hot solution of lactobionic acid results in the slow formation of a fine white precipitate. After eighteen hours' standing at room temperature the precipitate was filtered off and washed three times with cold water saturated with calcium hydroxide. This precipitate was then suspended in 100 cc. of water, neutralized with carbon dioxide and the bicarbonate decomposed by passing air through the warmed solution. The filtrate was concentrated to 50 cc. on the water-bath by a current of air, transferred to a mortar and rubbed with 250 cc. of 95% alcohol. The precipitated gummy mass of neutral calcium lactobionate soon became granular on further rubbing. It was triturated successively with 50-cc. portions of 80%, 95% and absolute alcohol, collected on a filter and dried at 80"; yield, 34.5 g. The precipitation

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[7] Rertrand, *Bull. soc. chim.*, 5, 554 (1891).

[8] C. A. Browne, "Inaugural Dissertation," Göttingen, 1901, p. 21.

[9] The hydrobromic acid may be more rapidly removed by using litharge in place of lead carbonate or by omitting lead entirely and using 28 g. of silver carbonate.

of lactobionic acid as its basic calcium salt by calcium hydroxide is not quite quantitative and it was possible by concentrating the mother liquor and adding alcohol to obtain about 3 g. more of an impure salt which reduced Fehling's solution slightly. Redissolving this in a little water and reprecipitating with alcohol purifies it. Three such purifications yielded 2.1 g. which contained no sugars. The total yield of neutral calcium lactobionate was thus 36.6 g. or 95.7% of the theoretical. The result shows that the procedure of bromine oxidation can be applied to compound reducing aldoses in a way that avoids hydrolysis and gives a nearly quantitative yield of the corresponding compound aldonic acid or its salts.

Hydrolysis of Lactobionic Acid to Galactose and Gluconic Acid.—It will be recalled that Fischer and Meyer[3] first carried out this hydrolysis and by it proved that lactose is a galactosidoglucose rather than a glucosidegalactose. So far as we are aware, the preparation has never been repeated though the beautiful reasoning from which the conclusion is deduced should appeal so strongly to students that the preparation might well be included in laboratory instruction. Doubtless the difficulties which Fischer records in preparing pure lactobionic acid have deterred others from repeating the work. It is believed that the directions which are now supplied improve the method to such an extent that it may be used generally by students.

A solution of 9 g. of calcium lactobionate in 100 cc. of 7.5% sulfuric acid was heated for three hours on the steam-bath and then neutralized with calcium carbonate (8 g.). The yellow solution was decolorized with carbon, filtered and concentrated under reduced pressure to 30 cc. The gradual addition of 70 cc. of hot methyl alcohol precipitated most of the calcium gluconate as a heavy sirup, the galactose remaining in solution. The liquid was decanted and the sirup was extracted thrice with 50 cc. of hot methyl alcohol. The alcoholic solutions were combined, purified with 1 g. of active carbon, filtered and evaporated to a sirup on a hot-plate by a current of air. Galactose crystallized from this sirup on standing overnight. It may be preferable to start crystallization by nucleation. The crystals were washed with 50% cold alcohol and dried at 65°; yield, 2.5 g. The mother liquor was concentrated to a sirup, which was dissolved in 50 cc. of hot methyl alcohol. A small quantity of insoluble material was filtered off and added to the calcium gluconate fraction. The alcoholic solution was concentrated as before and from it was obtained, after nucleation, 0.95 g. of crystalline galactose. The total yield of galactose was 3.45 g. or 80% of the theoretical. After one recrystallization from 10 cc. of hot water, the sugar showed a melting point of 165° and $[\alpha]^{20}_{D} = 79.7$ in aqueous solution.

The amorphous calcium gluconate was dissolved in 15 cc. of hot water and crystallized from the cooled solution by the addition of alcohol just short of cloudiness (about 5 cc.) and scratching the container. After standing overnight in an ice box the crystals were filtered off, washed with a little cold water and dried at 65°; yield, 4.8 g. The mother liquor yielded only 0.1 g. of crystals; total yield, about 95% of the theoretical. After one recrystallization and drying at 65° the salt showed $[\alpha]^{20}_{D} = +8.2$ in aqueous solution.

Summary

It is found that the use of a buffering salt of an organic acid, such as barium or calcium benzoate, during the oxidation of aldoses by bromine water, greatly increases the speed of the reaction, due to the maintaining

of a relatively low hydrogen-ion concentration and permits the oxidation of compound reducing aldoses, such as lactose, without complications from hydrolysis. The reaction mixture should be kept in the dark for best results. The yields of aldonic acid are nearly quantitative. In the case of lactose it is possible to oxidize it to nearly pure lactobionic acid, which can then be hydrolyzed to galactose and gluconic acid, both of which can be obtained in high yield. It is believed that the new directions make the method of bromine oxidation of aldoses much more precise and suitable for a wide range of preparations. Examples of the oxidation of glucose, xylose and lactose are given. It is suggested that the improved directions may be found suitable for laboratory instruction in sugar chemistry as well as for research.

WASHINGTON, D. C.

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

HALOGEN-SUBSTITUTED AROMATIC PINACOLS AND THE FORMATION OF KETYL RADICALS, $R_2(IMgO)C—$

BY M. GOMBERG AND JOHN C. BAILAR, JR.[1]

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It has been shown that aromatic ketones may be reduced to pinacols by a binary system consisting of a mixture of magnesium iodide and magnesium in anhydrous solvents[2]

$$2R_2CO \xrightarrow[Mg]{MgI_2} R_2(IMgO)C—C(OMgI)R_2 \xrightarrow{H_2O} R_2(HO)C—C(OH)R_2 + 2Mg(OH)I \quad (1)$$

We now find that this method can be applied to the preparation even of some of the halogenated pinacols with considerable success.

The decisive color effects given by some of our pinacols afforded an opportunity to test, by the application of Beer's law, the hypothesis that halomagnesium pinacolates dissociate into ketyls

$$R_2(IMgO)C—C(OMgI)R_2 \rightleftharpoons 2R_2(IMgO)C— \quad (2)$$

In the field of the pinacolin rearrangement, various investigators have reported upon the relative migratory tendency of bromophenyl and phenyl groups[3], and upon that of phenyl and biphenyl groups.[4] We have now studied the relative migratory tendencies of bromophenyl and biphenyl groups, in order to compare the actual findings with the predictions.

Preparation of the Halogen-Substituted Pinacols.—For preparative purposes, best results are obtained with tolerably concentrated solutions

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[1] The material here presented is from a dissertation submitted by John C. Bailar, Jr., to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1928.

[2] Gomberg and Bachmann, THIS JOURNAL, 49, 236 (1927).

[3] Montagne, *Rec. trav. chim.*, 29, 150 (1910); Koopal, *ibid.*, 34, 115 (1915).

[4] Ref. 2, p. 251.

of the ketones and magnesium iodide, and with the metal in the form of powder; the reduction is complete in a few hours, especially when the mixture is heated. However, for the study of the mechanism of the reaction, a modified procedure has been used in order to obtain further evidence whether the amount of magnesium consumed by the reduction fulfils the conditions of the hypothesis (Equation 1), and also in order to determine to what extent the halogen in the ketone molecule is detached from the benzene nucleus. Obviously, if no such halogen be split off, then for each equivalent of metallic magnesium consumed one equivalent of hydroxide ion should be formed on hydrolysis of the glycolate, and one mole of the ketone should be reduced to pinacol. On the other hand, if, in addition to reduction of the CO group, some halogen in the ring is removed, the amount of magnesium dissolved will be larger, and will be equivalent to the sum of the hydroxide ion and halide ion detached from the nucleus.

These measurements were carried out in the following manner. Somewhat more than 0.01 of a gram atom of iodine and an excess of magnesium powder were allowed to react in anhydrous ether, and the colorless solution was filtered into a 100-cc. graduate. Ordinarily most of the ether was boiled off and the solution was diluted to a known volume with dry benzene, retaining just enough ether to keep the magnesium iodide in solution. Two cc. of the solution was pipetted out and titrated for halide and the amount of the halide in the remaining solution was calculated. To this solution was added 0.01 of a gram molecule of the ketone and a weighed amount of magnesium shavings; the graduate was stoppered and shaken until the reaction was certain to have become complete. When the magnesium shavings remaining had settled, most of the liquid was pipetted off and quickly poured into water containing a known amount of standard sulfuric acid. The water layer was diluted to 500 cc. Of this, 100 cc. was titrated with sodium hydroxide and 25 cc. with silver nitrate. Simple calculation indicates how many equivalents of hydroxide ion have been produced by the hydrolysis of the pinacolate, and possibly other organomagnesium compounds, and how many equivalents of halide have been liberated from the ring. The magnesium shavings were filtered from the remaining liquid, quickly washed with ether, alcohol and water, then dried and weighed. The benzene layer was dried and allowed to evaporate. The product was macerated with petroleum ether or with alcohol in order to remove any unchanged ketone, and the pinacol remaining weighed.

It has been found that while *m*- and p-halogenated ketones are reduced to the corresponding pinacols, in the o-substituted ketones the halogen in the nucleus is also attacked by the magnesium. The reduction of the halogen-substituted ketones proceeds much more slowly than in the case of the ketones that Gomberg and Bachmann reduced. Instead of a few minutes, some of the bromobenzophenones are not completely reduced, even after shaking for several hours.

Gomberg and Bachmann reported that magnesium bromide can be substituted for the iodide in this reaction; the only difference is in the speed of the reduction. In the case of the halogenated benzophenones this does not seem to be the case. The conditions were varied widely in regard to concentration, time and temperature, but in every instance the ketone was recovered unchanged. This failure of magnesium bromide to react may be due to the extreme insolubility of the double compounds formed between the ketones and magnesium bromide.

Sym.-**4,4′-dibromobenzopinacol.**—This was prepared from 4-bromobenzophenone in accordance with the general directions. One one-hundredth of a mole of ketone gave rise to 0.009 equivalents (0.0045 mole) of the pinacol and 0.0093 equivalents of $(OH)^-$, and there was consumed 0.0095 equivalent of magnesium. No ring halogen was taken out by the metallic magnesium. In nearly all of the experiments, as in this one, slightly more than the theoretical quantity of magnesium was consumed. This discrepancy is explained if the formation of magnesium oxide, by the air left in the reaction vessel, is considered. When working with larger amounts and magnesium powder, the yield of pure product was 94%; and the crystals of the pinacol melted at 178°, as given by Montagne.

Sym.-**3,3′-dibromobenzopinacol.**—*m*-Bromobenzophenone gave with magnesium iodide a white double compound that did not completely dissolve until after three days. It was found that from 0.01 mole of ketone, 0.01 equivalent of pinacol had been produced, 0.0104 equivalents of magnesium had been used up, and no bromine had been removed from the benzene ring in the ketone molecule.

In another experiment 5.2 g. of the ketone was reduced in 60 cc. of solution in a few hours. The pinacol melted sharply at 147°, as Koopal has previously found. The yield of pure product was 85%.

Reduction of 2-Bromo- and of 2-Chlorobenzophenones by the Binary System.—The bromine atom of 2-bromobenzophenone is so labile that it may be removed almost completely from the molecule by the action of the magnesium and magnesium iodide mixture, although magnesium alone has no effect, even upon boiling for several days. It was never possible to get more than a very small amount of pinacol; this melted at 160–165°, as compared with 168° as given by Koopal.

A mixture of magnesium and magnesium bromide gave equally unsatisfactory results. In one experiment the vessel was heated to 70° for a week. The solution became pink but when the mixture was hydrolyzed it was found that no reduction had taken place, but that 17.5% of the ketone had been destroyed through loss of nucleus bromine.

2-Chlorobenzophenone behaves like its bromo-analog and repeated experiments indicated that a large amount of chlorine had been removed from the benzene nucleus.

This result with the o-halogeno-benzophenones is in harmony with other instances of lability of halogen atoms ortho to the carbonyl group. In addition to the well-known Ullmann syntheses from o-chlorobenzoic acid, one may mention the experience of Montagne and van Charante,[5] of Simonis and Kirschten[6] and of Zal'kind and Schmidt.[7]

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[5] Montagne and van Charante, *Rec. trav. chim.*, 31,300 (1912).

[6] Simonis and Kirschten, *Ber.*, 45, 567 (1912).

[7] Zal'kind and Schmidt, *J. Russ. Phys.-Chem. Soc.*, 46,681 (1914).

4,4′,4″,4‴-Tetrabromobenzopinacol.—Magnesium iodide and 4,4′-dibromobenzophenone form a yellow double compound. After six hours' shaking with metallic magnesium the precipitate was completely dissolved and the solution was clear bright red; after ten hours more it was hydrolyzed. The pinacol melted at 179–180°, as Montagne[8] has reported. The yield of pure product was 94%.

The quantitative relationships involved are normal. From the reaction with 0.01 mole of ketone there was obtained 0.0091 equivalent of pinacol and 0.0091 equivalent of magnesium were used **up.** No bromide ion was present in the aqueous solution.

3,3′-Dibromobenzophenone.—To the Grignard reagent from 20 g. of *m*-dibromobenzene and 2 g. of magnesium was added an ether solution of 15.4 g. of *m*-bromocyanobenzene. The solution was refluxed for several hours and then hydrolyzed. After three recrystallizations from alcohol, the ketone melted sharply at 140°.[9] The yield of pure material was 13.7 g. or 46%. From the mother liquors was obtained a small amount of a substance consisting of very fine needles, m. p. 172°, doubtless the diketone, *m*-$BrC_6H_4COC_6H_4COC_6H_4Br$-*m*, (CO:CO = 1:3).

Anal. Calcd. for $C_{13}H_8OBr_2$: Br, 47.06. Found: Br, 47.20. *Mol. wt.* in benzene. Calcd.: 340. Found: 341. *Anal.* of diketone. Calcd. for $C_{20}H_{12}O_2Br_2$: Br, 36.04. Found: Br, 35.70.

3,3′,3″,3‴-Tetrabromobenzopinacol.—In the process of reduction the solution assumed a bright red color and after five days the double compound, ketone + MgI_2, had completely dissolved. The pinacolate was hydrolyzed in the usual way; it was found that no halogen had been removed from the ketone molecule and that the calculated amount of magnesium was used up. The pinacol was exceedingly difficult to purify and only 40% of the crystalline product could be obtained pure. After recrystallization from a mixture of alcohol and chloroform, it melted at 152–156°.

Anal. Calcd. for $C_{26}H_{18}O_2Br_4$: Br, 46.92. Found: Br, 46.99. *Mol. wt.* in benzene. Calcd.: 682. Found: 658.

3,4′-Dibromobenzophenone.—A mixture of 20 g. of 3-bromobenzoyl chloride, 50 cc. of bromobenzene and 14 g. of aluminum chloride was heated on the steam-bath for three days. The ketone was recrystallized from alcohol and then from benzene; the yield was 49%; m. p. 132°.[10]

For the purpose of verifying the constitution, the same ketone was prepared by the Grignard reaction, from *p*-dibromobenzene and m-bromocyanobenzene. After successive recrystallizations from benzene, acetone and alcohol, pure ketone was obtained, m. p. 130–131°. Mixed with the product obtained by the method of Friedel and Crafts, it melted at the same temperature. Here again a small amount of the diketone, *m*-$BrC_6H_4COC_6H_4COC_6H_4Br$-*m*, was formed (CO:CO = 1:4); m. p. 217–220°.

Anal. Calcd. for $C_{13}H_8OBr_2$: Br, 47.06. Found: Br, 47.09. *Mol. wt.* in benzene. Calcd.: 340. Found: 343. *Anal.* of diketone. Calcd. for $C_{20}H_{12}O_2Br_2$: Br, 36.04. Found: Br, 36.47.

Sym.-**3,3′,4,″4‴-Tetrabromobenzopinacol.**—The reduction of 3,4′-dibromobenzophenone proved to be a very difficult problem, although the **4,4′-dibromo-** and the 3,3′-dibromobenzophenones offered no difficulty. **A** solution of a large excess of magnesium iodide, from 8 g. of iodine and an excess of magnesium powder, in 50 cc. of ether was diluted to 100 cc. with benzene and 1 g. of the ketone was added. The vessel was tightly stoppered and the solution was heated to 75° for four days. At the end

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[8] Montagne, Rec. *trav. chim.*, 43, 640 (1924).

[9] Demuth and Dittrich, *Ber.*, **23,** 3614 (1890).

[10] Kunckell, *ibid.*, 37,3485 (1904).

of the first day a pink color had developed—this gradually darkened to deep red. Although the reduction had proceeded to the extent of 76%, only about 35% of the material could be obtained crystalline; m. p. 160–163°. No bromine was detached from the ketone.

Anal. Calcd. for $C_{26}H_{18}O_2Br_4$: Br, 46.92. Found: Br, 47.17. Mol. *wt.* in benzene. Calcd.: 682. Pound: 686.

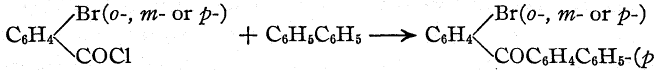
4-Chloro-4'-bromobenzophenone.—This ketone was prepared from 4-bromobenzoyl chloride, chlorobenzene and aluminum chloride. After recrystallization from alcohol and then from benzene it melted at 150°. The yield of pure product was 60%. The identical ketone was also prepared from 4-chlorobenzoyl chloride and bromobenzene.

Anal. Calcd. for $C_{13}H_8OBrCl$: Br, 27.07; Cl, 12.01. Found: Br, 27.46; Cl, 11.85. Mol. *wt.* in benzene. Calcd.: 295.5. Found: 289.

Sym.-**4,4'-dichloro-4'',4'''-dibromobenzopinacol.**—With magnesium shavings the reduction is somewhat slow, but after eight hours' shaking with magnesium powder the yield of the pinacol is quantitative. The halogen in the benzene nucleus is not affected by the metallic magnesium. The pinacol is crystallized from ether or acetone and melts at 169°.

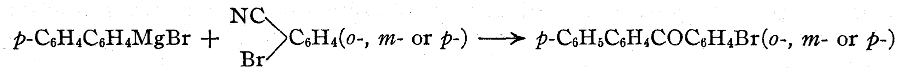
Anal. Calcd. for $C_{26}H_{18}O_2Br_2Cl_2$: Br, 26.98; Cl, 11.97. Found: Br, 26.52; Cl, 12.26. Mol. *wt.* in benzene. Calcd.: 593. Found: 633.

4-Bromo-4'-phenylbenzophenone, 3-Bromo-4'-phenylbenzophenone **and** 2-Bromo-**4'-phenylbenzophenone.**—These three ketones were prepared according to the reaction



$$C_6H_4{<}\begin{matrix}Br(o\text{-}, m\text{- or } p\text{-})\\ COCl\end{matrix} + C_6H_5C_6H_5 \longrightarrow C_6H_4{<}\begin{matrix}Br(o\text{-}, m\text{- or } p\text{-})\\ COC_6H_4C_6H_5\text{-}(p)\end{matrix}$$

The acid chloride from 20 g. of the corresponding bromobenzoic acid was dissolved in 150 cc. of carbon disulfide, 20 g. of biphenyl was added, and then 16 g. of aluminum chloride, in small portions. The mixture was warmed on the steam-bath for three days. After hydrolysis, the unchanged biphenyl was removed by distillation under reduced pressure. The ketones may then also be distilled under reduced pressure, though their boiling points are very high (near 300° at 15–18 mm.), or they may be purified by crystallization from alcohol or benzene. The yields were *o*-bromo-, 65; m-, 75 and *p*-, 55%. In order to verify the structure of the ketones they were prepared also from *p*-biphenylmagnesium bromide and the corresponding bromocyanide



$$p\text{-}C_6H_4C_6H_4MgBr + \begin{matrix}NC\\ Br\end{matrix}{>}C_6H_4(o\text{-}, m\text{- or } p\text{-}) \longrightarrow p\text{-}C_6H_5C_6H_4COC_6H_4Br(o\text{-}, m\text{- or } p\text{-})$$

The materials prepared by the two different methods melted at the same temperature in every case and mixed melting points showed no depression. The melting points, analyses and molecular weights are:

Ketone, $C_9H_{13}OBr$	M. p., °C.	Bromine Calcd.	Bromine Found	Mol. wt. Calcd.	Mol. wt. Found
Ortho	88.5	23.74	23.84	337	343
Meta	119		23.74		339
Para	188		23.55		334

Sym.-**4,4'-Dibromo-4'',4'''-Diphenylbenzopinacol.**—4-Bromo-4'-phenylbenzophenone, subjected to the action of the binary system, gave a light green solution of the ketyl. No bromine had been removed from the ketone molecule. The loss in weight of the magnesium and the amount of pinacol corresponded each to 0.009 equivalent. The pinacol melts at 158–159°.

Anal. Calcd. for $C_{38}H_{28}O_2Br_2$: Br, 23.67. Found: Br, 23.56. *Mol. wt.* in benzene. Calcd.: 676. Found: 652,

Sym.-**3,3′-Dibromo-4″,4‴-Diphenylbenzopinacol.**—This was obtained by reduction of the 3-bromo-4'-phenylbenzophenone in a solution containing largely benzene and but little ether. The yield of pinacol was 64%; m. p. 175°.

Anal. Calcd. for $C_{38}H_{28}O_2Br_2$: Br, 23.67. Found: Br, 23.63. *Mol. wt.* in benzene. Calcd.: 676. Found: 662.

Reduction of 2-Bromo-4'-Phenylbenzophenone.—This ketone, which contains a bromine atom ortho to the carbonyl group, offered the same difficulties as the 2-bromo- and 2-chlorobenzophenones. Bromine was removed from the ketone and no pinacol could be isolated.

Colorimetric Study of the Iodomagnesium Pinacolates

The iodomagnesium pinacolates are colorless in the solid state but when dissolved impart color to the solution. In this respect they behave very much like so many of the hexa-arylethanes, and, like the latter, they are assumed to dissociate with the production of free radicals; in this case the ketyls of the type $R_2C(OMgI)$, Equation 2. Unfortunately, it has not proved possible to isolate the pinacolates in such a degree of purity that molecular weight determinations could serve as definite proof of their dissociation. We have therefore sought to determine whether the color of solutions of pinacolates is intensified on dilution. Such deviation from Beer's law has, in many cases, furnished the only means of detecting changes on dilution, that is, dissociation into free radicals. Four iodomagnesium pinacolates, namely, those prepared from benzophenone, 4-bromobenzophenone, 4-chloro-4'-bromobenzophenone and 4-bromo-4'-phenylbenzophenone, have been studied from the point of view of Beer's law. The solutions of all of these pinacolates are red.

We have used the colorimeter previously described,[11] but so modified for the present purposes that, instead of solid pinacolates, the reduction solutions of the ketones could be introduced directly into the colorimeter. The ketone was reduced by means of the binary system in a Drechsel bottle; one arm of this was then connected with appropriate stopcocks to a hydrogen pressure tank and the other led to a filtering tube, from which the pinacolate solution could be discharged into each of the two comparator tubes and into the reservoir.

The iodomagnesium pinacolates are extremely sensitive to traces of air and great care was necessary in order to avoid decolorization of the solution. The entire system was repeatedly evacuated and filled with hydrogen. During the course of the experiment the apparatus was always kept under a positive pressure of hydrogen. All rubber connections were made of the best material available and were coated at the joints

[11] Gomberg and Sullivan, THIS JOURNAL. 44, 1825 (1922).

with paraffin or de Khotinsky cement. In some of the earlier experiments the filtering funnel was fitted with hardened filter paper instead of the alundum disk, as in the latter experiments, but it was found that the traces of air adsorbed by the paper were sufficient to decolorize a dilute solution of the pinacolate. The hydrogen was purified by passing over a red-hot copper spiral and through concentrated sulfuric acid. The solvent used for diluting the solutions was freed from dissolved air by bubbling pure hydrogen through it. Part of the pinacolate solution was forced through the filter tube into that arm (B) of the colorimeter where dilutions were to be made, the remainder into the reservoir. The liquid in the reservoir could then be raised into the second arm (A) of the colorimeter by pressure of hydrogen until the depth of color appeared the same in the two colorimeter tubes. Solvent was then forced into the colorimeter tube B and, when equilibrium had been established, the

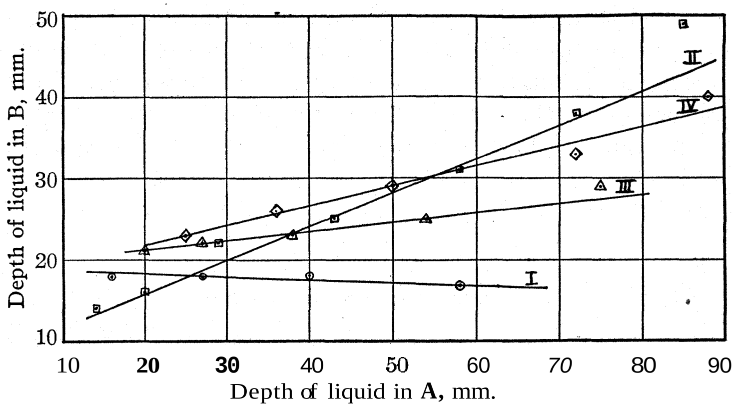
TABLE I

CHANGE OF COLOR WITH DILUTION

Benzopinacolate Depth in mm.		*Sym.*-4,4′-dibromobenzopinacolate Depth in mm.		*Sym.*-4,4′-dichloro-4″,4‴-dibromobenzopinacolate Depth in mm.		*Sym.*-4,4′-dibromo-4″,4‴-diphenylbenzopinacolate Depth in mm.	
B	A	B	A	B	A	B	A
Ketone—7.5 g.		Ketone—1 g.		Ketone 4 g.		Ketone—4 g.	
Iodine—7.5 g.		Iodine—1.5 g.		Iodine 4 g.		Iodine—4 g.	
15	14	14	8	20	21	23	22
24	13	29	12	27	22	33	26
37	13	45	17	38	23	52	35
55	11	58	19	54	25	65	40
		73	27	75	29		
Ketone—3 g.		Ketone—1 g.		Ketone--4 g.		Ketone—4 g.	
Iodine—3 g.		Iodine—1.5 g.		Iodine 4 g.		Iodine—4 g.	
16	18	10	10	18	19	25	23
27	18	25	16	34	22	36	26
40	18	38	17	48	25	50	29
58	17	50	20	74	31	72	33
		64	22			88	40
Ketone—2 g.		Ketone–1 g.				Ketone—7.5 g.	
Iodine—2 g.		Iodine—1.5 g.				Iodine—7.5 g.	
28	30	14	14			19	16
34	32	20	16			28	19
40	33	29	22			37	23
48	33	43	25			49	26
		58	31			68	28
Ketone—10 g.		72	38				
Iodine—10 g.		85	49				
22	22	Ketone 4 g.					
29	22	Iodine 4 g.					
38	20	22	22				
50	22	30	25				
		44	31				

depth of color in the two tubes was again compared and another dilution was made. The average of four or more readings is recorded in the table, the individual readings agreeing within one mm.

The results of typical experiments on each of the ketones studied are shown graphically in Fig. 1. They show unmistakably that in three of the four cases increase of color occurs. Consequently, the pinacolates dissociate on dilution, producing iodomagnesium ketyls.

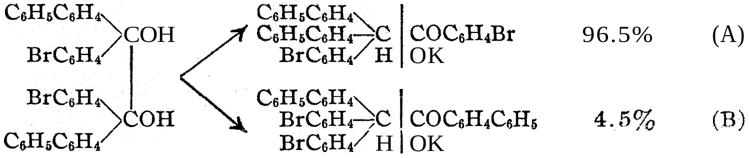


I, ⊙, Benzopinacolate; II, ⊡, 4-4′-dibromo-*sym.*-benzopinacolate; III, △, 4-4′-dichloro-4″,4‴-dibromo-*sym.*-benzopinacolate; IV, ◇, 4-4'-dibromo-4", 4‴-diphenyl-*sym.*-benzopinacolate.

Fig. 1.

Comparative Migratory Tendencies of the Phenyl, p-Biphenyl, p-Bromophenyl and m-Bromophenyl Groups.—Montagne[3] has compared the migratory tendencies of the p-bromophenyl and the phenyl groups by rearranging the appropriate pinacol, and has found that 42 to 43% of the rearrangement is due to the migration of the p-bromophenyl group and 57 to 58% to that of the unsubstituted phenyl group. This work has been repeated and Montagne's results have been checked; our results have shown 41% of the migration due to the bromophenyl group and 59% to the phenyl group. Koopal has compared the migratory tendencies of the phenyl and the m-bromophenyl groups and has reported that only the substituted group migrates. This result has also been substantiated. Gomberg and Bachmann have shown that in the rearrangement of 4,4′-*sym.*-diphenylbenzopinacol, 92% of the migration is due to the *p*-phenylphenyl group and 8% to the unsubstituted group. Taking the migratory tendency of the phenyl group as 1, we may arrange the other groups as follows: p-bromophenyl, 0.695; m-bromophenyl, 0; p-phenyl-phenyl, 11.5. From these one may predict that the migratory tendencies of the *p*-bromophenyl and p-phenyl-phenyl groups should be in the relation of 1:16.5. Also, in a pinacol with a m-bromophenyl and p-phenyl-phenyl group, the latter group exclusively will migrate in the pinacolin rearrangement. Our actual results gave for the first case, 21.5 instead of 16.5; for the second, complete corroboration.

Rearrangement **of** ***Sym.*-4,4'-Dibromo-4'',4'''-Diphenylbenzopinacol.**—Two grams



of the pinacol was dissolved in a mixture of 40 cc. of benzene, 10 cc. of acetic acid and 20 cc. of acetyl chloride, and the solution was boiled gently for eight hours. The liquid was evaporated and the crystalline residue of the pinacolins was boiled twelve hours with alcoholic potassium hydroxide. After removal of the triarylmethane compound, the resulting acids were separated from each other by converting the phenylbenzoic acid into the insoluble barium salt. We obtained 0.038 g. of this salt (which is equivalent to 0.028 g. of the phenylbenzoic acid) and 0.589 g. of bromobenzoic acid. This corresponds to 4.5 and 96.5%, respectively. The migratory tendencies are as 1:21.5. The pinacolin (A), recrystallized from glacial acetic acid, melts at 227°.

Anal. Calcd. for $C_{38}H_{26}OBr_2$: Br, 24.32. Found: Br, 23.97. *Mol. wt.* in benzene. Calcd.: 658. Found: 637.

The methane compound that was obtained by the splitting of the pinacolin was recrystallized from glacial acetic acid and melts at 186°. Since this substance has not been described, it was synthesized from biphenyl-p-magnesium bromide and the methyl ester of *p*-bromobenzoic acid. The 4,4'-diphenyl-4''-bromotriphenylcarbinol that resulted melted at 248–250°; reduced by means of zinc and glacial acetic acid, it gave the methane, which after purification melted at 186°. Rearrangement of the pinacol by acetic acid and iodine gave the same pinacolin.

Anal. of Carbinol. Calcd. for $C_{31}O_{23}OBr$: Br, 16.29. Found: Br, 16.03. ***Anal.*** of Methane. Calcd. for $C_{31}H_{23}Br$: Br, 16.84. Found: Br, 17.20. ***Mot.*** wt. in benzene. Calcd.: 475. Found: 497.

Rearrangement **of** ***Sym.*-3,3'-Dibromo-4'',4''-Diphenylbenzopinacol.**—This rearrangement was carried out with 2 g. of pinacol in the same way as that of the 4,4'-dibromo-4'',4'''-diphenylbenzopinacol. The pinacolin gave only 0.002 g. of *m*-bromobenzoic acid, which is practically negligible. Thus the rearrangement is due entirely to the migration of the *p*-phenyl-phenyl group. The pinacolin, recrystallized from glacial acetic acid, melts at 202–203'.

Anal. Calcd. for $C_{38}H_{26}OBr_2$: Br, 24.32. Found: Br, 24.14. ***Mol. wt.*** in benzene. Calcd.: 658. Found: 652.

The constitution of the methane compound as 4,4'-diphenyl-3''-bromotriphenylmethane was verified by preparing it from the m-bromobenzoic ester exactly as was described for the b-bromomethane. The carbinol melted at 304° and the methane at 143°.

Anal. of Carbinol. Calcd. for $C_{31}H_{23}OBr$: Br, 16.29. Found: Br, 16.58. ***Anal.*** of Methane. Calcd. for $C_{31}H_{23}Br$: Br, 16.84. Found: Br, 16.70. ***Mol.*** wt. in benzene. Calcd.: 475. Found: 469.

This investigation has been carried out with the aid of a fellowship donated by the University of Michigan. We wish to express our gratitude for the aid so received.

Summary

1. It has been shown that the method suggested by Gomberg and Bachmann can be applied to the preparation of many halogeno-benzopinacols, especially those from ketones containing bromine or chlorine atoms meta or para to the CO group. When the halogen atom is in the ortho position, however, the magnesium of the reducing mixture tends to remove the halogen atom from the ketone molecule and no pinacol is formed.

2. By a study of the iodomagnesium pinacolates from the point of view of Beer's law, the existence of the equilibrium pinacolate   ketyl, has been demonstrated.

3. The relative migratory tendencies of the p-bromophenyl, *m*-bromophenyl and p-phenyl-phenyl groups have been determined by rearrangement of the appropriate pinacols to pinacolins. The results obtained are in good agreement with those obtained by previous investigators on different examples.

ANN ARBOR, MICHIGAN

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

REDUCTION OF AROMATIC 1,2-DIKETONES BY THE BINARY SYSTEM MAGNESIUM IODIDE (OR BROMIDE) + MAGNESIUM

BY M. GOMBERG AND F. J. VAN NATTA[1]

RECEIVED MARCH 27, 1929 PUBLISHED JULY 5, 1929

Benzil is reduced by the binary system[2] to the unsaturated glycolate, iodomagnesium-stilbene–diolate, $C_6H_5(IMgO)C{=}C(OMgI)C_6H_5$, which when hydrolyzed gives benzoin. We have now extended this reaction to various benzils and find that it may be applied even to halogen-substituted diketones without danger of removing the halogen. Many of the reactions of the new unsaturated glycolates are analogous to those of the parent substance. More definite evidence, however, has now been obtained in regard to the reaction between the diketones and MgI_2 alone. It was reported that benzil liberates iodine from MgI_2, presumably in accordance with the reaction

$$RCOCOR + 2MgI_2 \rightleftharpoons R(IMgO)C{=}C(OMgI)R + I_2 \qquad (1)$$

About 5% of the calculated amount of iodine was found to be set free but most careful search failed to reveal benzoin in the hydrolyzed reaction product. Experience with substituted, more reactive, benzils here described has now definitely proved the correctness of that hypothesis.

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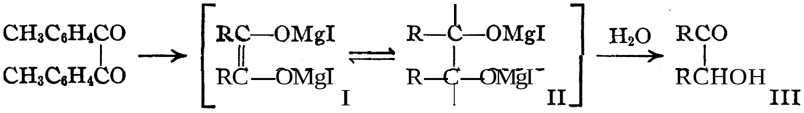
[1] The material here presented is part of a dissertation submitted by F. J. Van Natta to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1928.

[2] Gomberg and Bachmann, THIS JOURNAL, 49,2584 (1927).

When a diketone is added to the binary system, there is consequently liberation of some iodine from the magnesium iodide, with simultaneous formation of an equivalent amount of the unsaturated iodomagnesium glycolate. As reduction proceeds through the presence of the metallic magnesium, the red solution becomes still deeper in color, notwithstanding the fact that the iodine is being taken up by the metal. Later in the process the solution commences to lighten. While the reduction of benzil itself gave an almost colorless solution of the glycolate, the solutions which resulted on the reduction of substituted benzils are usually quite intensely colored. The loss in weight of metallic magnesium convinced us that all of the ketone had been reduced; quinhydrone formation between glycolate and unreduced ketone is, consequently, excluded. This persistence of color we are inclined to interpret by the supposition that we have here a partial opening of the double bond in the unsaturated glycolate, forming a single bond with the production of two trivalent carbon atoms. I $\rightleftharpoons$ II.[3] Those glycolates especially which contain methoxyphenyl and biphenyl groups give deep colors—an indication of the extent to which C^{III} is produced. This behavior is in harmony with the extensive formation of free radicals from those hexa-arylethanes, tetra-arylhydrazines and tetra-aryldicyano-ethanes[4] which contain either anisyl or biphenyl groups.

Reduction of *p*-Tolil by the Binary System



$$\begin{array}{c}CH_3C_6H_4CO\\ |\\ CH_3C_6H_4CO\end{array} \longrightarrow \left[\begin{array}{c}RC—OMgI\\ \|\\ RC—OMgI\end{array}_{\text{I}} \rightleftharpoons \begin{array}{c}|\\ R—C—OMgI\\ |\\ R—C—OMgI^-\\ |\end{array}_{\text{II}}\right] \xrightarrow{H_2O} \begin{array}{c}RCO\\ |\\ RCHOH\end{array}_{\text{III}}$$

The solution of magnesium iodide was prepared from 2.5 g. (0.02 atom) of iodine and 0.5 g. of magnesium powder in a mixture of 25 cc. of ether and 20 cc. of benzene; it was filtered from the excess of magnesium into a 70-cc. test-tube. To this solution was added 1.19 g. (0.005 mole) of tolil, and a weighed magnesium rod was inserted, followed by the addition of 20 cc. of benzene. The tube was tightly corked and placed on the shaking machine. In the course of several days the solution underwent the color changes deep red, light red and light brown. The transparent brown solution at this stage is very sensitive toward oxygen, the surface becoming opaque when exposed to air for an instant. The magnesium rod was removed, washed with benzene and reweighed. The solution was quickly decomposed with water, the precipitated magnesium hydroxide dissolved in standard sulfuric acid and the excess of acid titrated with standard alkali.

Anal. Loss in wt. of Mg, calcd.: 0.1216. Found: 0.1268. $Mg(OH)_2$ (in equivalents), calcd.: 0.01 equiv. Found: 0.0101 equiv.

The ether–benzene solution, which contained the hydrolyzed reduction product,

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[3] Schlenk and Weickel, *Ber.*, 44, 1189 (1911); Ingold and Marshall, *J. Chem. Soc.*, 129, 3081 (1926).

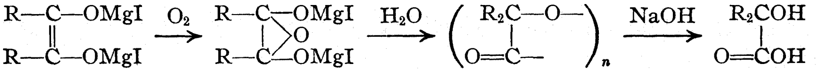
[4] Löwenbein and Gagarin, *Ber.*, 58, 2643 (1925); Blicke, THIS JOURNAL, 47, 1477 (1925).

was dried over sodium sulfate and evaporated spontaneously. The 1.15 g. of crystalline product consisted mainly of toluoin in admixture with a small amount of tolil. By fractional crystallization from hot alcohol the two products may be separated, but not quantitatively. For the estimation of the relative amounts of toluoin and tolil, the mixture in alcohol was boiled with excess of Fehling's solution and the amount of cuprous oxide, due to reduction by the toluoin, was determined. One mole of toluoin reduces two moles of cupric hydroxide. The reduction mixture from the 1.19 g. of tolil was in this manner found to consist of 77% of toluoin and 23% of tolil. In a separate experiment when hydrolysis was accomplished by means of boiled water and in a stream of nitrogen, the yield of toluoin was over 90%.

Reaction with Iodine and with Bromine.—The completely reduced solution of the glycolate, prepared as before from 1.19 g. of tolil, was treated with an equivalent amount of solid iodine and allowed to stand for two weeks. The reaction mixture was decomposed with dilute sulfuric acid and the free iodine titrated with sodium thiosulfate; about 52% of the iodine originally added was still present as such. Analysis by Fehling's solution showed the formation of an amount of tolil equivalent to the amount of iodine consumed. Evidently the reaction (Equation 1) reaches equilibrium when 48% of the glycolate has been oxidized.

With bromine the bromomagnesium glycolate reacted far more readily than with iodine, the end reaction being readily recognized and reached in a few minutes. The yield of tolil was over 90%.

Reaction with Dried Air



. The reduction of 1.19 g. of tolil was carried out in a corked Drechsel bottle. A slow stream of dried air was then passed through this solution, which soon became opaque; a large amount of free iodine separated. The mixture was hydrolyzed and worked up as with benzil. There were obtained 0.33 g. of the insoluble polymer, which accounts for 28% of glycolate oxidized, 0.54 g. of tolil and 0.32 g. of toluoin, which accounts for further 45% glycolate oxidized and for 27% glycolate which remained unaffected by the oxygen. The polymer shows no indication of melting below 360". On hydrolysis in the cold by aqueous potassium hydroxide it yields *p*-tolilic acid, m. p. 133–135°.[5]

p,p'-Dimethylstilbenediol-dibenzoate.—To a solution of the glycolate, from 2.38 g. of tolil, there was added 6 g. of benzoyl chloride and the mixture was allowed to stand for a short time. It was then decomposed with water and the product isolated in the usual manner. Crystallization of the crude ester from hot alcohol produced colorless needles of the dibenzoate; m. p. 135"; yield, 59%.

Anal. Calcd. for $C_{30}H_{24}O_4$: C, 80.36; H, 5.36. Found: C, 80.14; H, 5.43. Mol. *wt.* in benzene, calcd.: 448. Found: 442.

Reaction of Tolil with Magnesium Iodide Alone (Equation I).—To a filtered solution of 3.8 g. of magnesium iodide was added 1.19 g. of tolil. The resulting garnet-colored solution soon became turbid; within a half hour the tube was opaque. After standing in the dark for a month, the reaction mixture was decomposed with water. Titration with sodium thiosulfate showed the presence of 42% of the theoretical amount of iodine and analysis of the organic material showed that an equivalent amount of toluoin was produced.

Reduction by Magnesium Bromide and Magnesium.—To an ether solution of

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[5] Gattermann, Ann., 347, 364 (1906).

magnesium bromide[6] in a 70-cc. test-tube was added 4.76 g. of tolil and 20 cc. of benzene. A deep yellow solution resulted with no trace of insoluble double compound. No bromine is liberated, in contrast to the liberation of iodine from the reaction between magnesium iodide and tolil. A weighed magnesium rod was inserted and the tube was corked. Soon a deep brown coloration formed around the ends of the magnesium rod; after several hours the entire solution had become very deep brown. The reduction was apparently complete after twenty hours' shaking. The amount of magnesium used up in the reduction and that of the magnesium hydroxide formed on hydrolysis of the glycolate agreed satisfactorily with the calculated values. A yield of 82% of pure toluoin was obtained.

Reduction of p-Anisil

Anisil, 1.35 g., was added to a solution of magnesium iodide and immediately there formed, as an oil, an orange double compound. A weighed magnesium rod was then inserted and the tube stoppered. In the course of two days the solution became very deep red, and finally red in color, the double compound having disappeared. It was not possible to obtain a completely colorless solution even after three weeks, the final color being garnet-red.

The magnesium rod had lost 0.1249 g. (calcd. loss, 0.1216 g.) and the theoretical amount of magnesium hydroxide was formed on hydrolysis of the glycolate. By analysis with Fehling's solution, 62% of the theoretical amount of anisoin was shown to be present; the low yield is attributed to the fact that the reduction product, being extremely sensitive toward oxygen, is reoxidized in air to anisil.

With magnesium bromide solution, anisil forms a deep yellow insoluble addition compound; due presumably to the insolubility of this compound, it was not possible to reduce anisil in the cold by the system, $MgBr_2 + Mg$, even on prolonged contact of the reactants.

Reactions of the Glycolate.—After twelve days' reaction with the theoretical amount of iodine, equilibrium (Equation 1) was reached, and the reaction had proceeded to the extent of 63%. Also, when anisil was treated with magnesium iodide in ether solution, there was liberation of iodine with formation of glycolate to the extent of about 20%.

Air was passed into a solution of the glycolate for three days; much iodine was liberated. From the hydrolyzed reaction mixture there was isolated the polymerized acid anhydride, 31%, a cream-colored insoluble substance, infusible below 360". Hydrolysis of this material by alkalies produced anisilic acid; m. p. 175".

Reduction of *p,p'*-Dichlorobenzil

The crude benzoin, prepared by the condensation of *p*-chlorobenzaldehyde by means of potassium cyanide, showed no tendency toward crystallization even after extraction of the benzene solution with sodium bisulfite and subsequent evaporation of the benzene. Consequently, the mixture was oxidized directly by means of nitric acid diluted with acetic acid. After purification and recrystallization of the crude benzil from glacial acetic acid, pure *p,p'*-dichlorobenzil was obtained; m. p. 195–196°.

Reduction by Magnesium Iodide and Magnesium.—To a solution of magnesium iodide was added 1.40 g. of the benzil and a weighed magnesium rod. Iodine was liberated and during the course of two days' shaking the color of the solution changed from deep brown to light cherry-red; the magnesium rod had lost in weight the theoretical amount. The mixture was hydrolyzed, the organic solvent was evaporated, and the dichlorobenzoin and benzil were separated from each other by means of cold

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[6] Gomberg and Bachmann, THIS JOURNAL, 49, 245 (1927).

alcohol, the former being very much more soluble than the latter; in this way 9% of the benzil and **91%** of the benzoin were isolated. After recrystallization from dilute alcohol, the dichlorobenzoin melted at **85–87".** Hantzsch[7] reports the m. p., 88°.

Careful tests of the original aqueous washings from the reaction mixture failed to show the presence of any chloride ion. The nuclear chlorine atoms in the para position to the C=O group do not, then, react with metallic magnesium under the conditions of this experiment.

Attempts were made to reduce this benzil at room temperature by means of the system, $MgBr_2 + Mg$, but owing to the slight solubility of the benzil + $MgBr_2$ double compound, there was no reduction, and over **90%** of the benzil originally taken was recovered unchanged.

Reactions of the Glycolate.—With the theoretical amount of iodine after two weeks' shaking in the cold, the mixture was found to consist of equal parts of dichlorobenzil and of benzoin.

After two days' passage of air through a solution of it, the glycolate yielded **52%** of the white, insoluble anhydride of dichlorobenzilic acid polymer, **26%** dichlorobenzoin and **22%** of the benzil. The amorphous polymer decomposes at 320–340°; it gives a brilliant carmine color with concentrated sulfuric acid, identical with that shown by pure dichlorobenzilic acid.

p,p'-Dichlorostilbene-diol-dibenzoate.—After two recrystallizations from a mixture of benzene and alcohol, the product melted at 200–202°.

Anal. Calcd. for $C_{28}H_{18}O_4Cl_2$: Cl, **14.52.** Found: **Cl, 14.63.** *Mol. wt.,* calcd.: **489.** Found: **499.**

Reduction with Magnesium Iodide Alone.—The equilibrium: dichlorobenzil + $MgI_2 \rightleftharpoons$ glycolate + I_2, was attained when 62% of the benzil had reacted and formed the unsaturated glycolate.

Reduction of a-Naphthil

a-Naphthoin, $C_{10}H_7COCH(OH)C_{10}H_7$.—This product may be prepared by either of two methods: from a-naphthaldehyde, using potassium cyanide as a catalyst; or from a-naphthoic acid by reduction with magnesium iodide and magnesium powder in ether–benzene solution.[8] The solution, composed of **26.5** g. of a-naphthaldehyde, **10** g. of potassium cyanide, **100** cc. of alcohol and **50** cc. of water. was refluxed on the steam-bath for three hours; 5 g. more of potassium cyanide was added and the heating continued for eight hours. The solution was diluted with water and the organic material extracted with benzene. The benzene was evaporated and the residue, an oil, was redissolved in ether; on slow evaporation of the solvent, **3.4** g. of crystalline a-naphthoin was deposited. After recrystallization from hot alcohol, it melted at 138–139°.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.02; H, **5.13.** Found: **C, 84.51;** H, **5.14.**

The oil obtained on evaporation of the ether washings was oxidized to naphthil by copper sulfate in pyridine,[9] and **3.4** *g.* of naphthil was obtained as yellow prisms; m. p. 188–189°.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, **85.16;** H, **4.52.** Found: C, **84.87;** H, **4.55.** **Mol.** *wt.,* calcd.: **310.** Found: **329.**

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[7] Hantzsch and Glower, *Ber.,* **40, 1519 (1907);** Kenner and Witham, J. *Chem. Soc.,* **97, 1967 (1910).**

[8] Gomberg and Bachmann, THIS JOURNAL, **50,2767 (1928).**

[9] Clarke and Dreger, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1926,** Vol. **VI,** p. **6.**

The combined amount of naphthoin and naphthil obtained represented a yield of 26%, calculated on the amount of aldehyde taken.

The preparation of naphthoin from the acid is preferable to that from the aldehyde, as the acid is more accessible and the yield of naphthoin is somewhat larger.

The a-naphthil has previously been described by Stolle[10] who obtained it by the thermal decomposition of azo-dinaphthoyl, but in poor yield, owing to numerous side reactions. Quite recently Schlenk[11] described another method for the preparation of this substance. Our product agrees in its properties with those reported by these investigators.

The qninoxaline of a-naphthil, prepared by heating the diketone with *o*-phenylenediamine hydrochloride in pyridine, melts at 203–204°; color reaction with sulfuric acid, deep indigo-blue.

α-Naphthilic Acid $(C_{10}H_7)_2C(OH)CO_2H$.—This acid was prepared in good yield from a-naphthil by means of cold alcoholic potash in absolute ether solution.[12] It was recrystallized from benzene and petroleum ether; needle-like prisms, m. p., 137–138°, with decomposition. With concentrated sulfuric acid, naphthylic acid gives only a very slight brown color, while other benzilic acids produce brilliant colors.

Anal. Calcd. for $C_{22}H_{16}O_3$: C, 80 49; H, 4.88. Found: C, 80.76; H, 4.95. *Mol. wt.*, calcd.: 328. Found: by the ebullioscopic method, 330: by ignition of the Ag salt, 328.

Reduction of **α-Naphthil** by Magnesium Iodide and Magnesium.—The reduction was completed within three days. During this time, the mixture, originally deep red, became opaque, but the color finally lightened to a yellow. The magnesium rod had lost 97.6% of the theoretical amount. In order to minimize oxidation, the benzene solution was decomposed with boiled water in a stream of carbon dioxide and then the yield of pure a-naphthoin was 91%.

When dried air was allowed to pass for some time through a solution of the glycolate and the solution hydrolyzed, there was complete absence of the usual formation of the polymer-anhydride. Instead, there was formed naphthilic acid to the extent of 40%.

Reduction of *p,p'*-Diphenylbenzil

***p,p'*-Diphenylbenzoin,** $(C_6H_5C_6H_4)(HO)HCCO(C_6H_4C_6H_5)$.—A solution of 8 g. of *p*-phenylbenzaldehyde and 3 g. of potassium cyanide in 80 cc. of alcohol and 40 cc. of water was refluxed for two hours. A thick precipitate of the benzoin formed within fifteen minutes. The yield of the purified product was 95%. The diphenylbenzoin is soluble, 1 g. in about 115 cc. of cold benzene or ethyl acetate; it is quite soluble in hot pyridine, glacial acetic acid and xylene, and from these it may be obtained as a white powder; m. p. 168–170°.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.71; H, 5.50. Found: C, 85.42; H, 5.50. *Mol. wt.*, calcd.: 364. Found: 375.

***p,p'*-Diphenylbenzil,** $(C_6H_5C_6H_4)COCO(C_6H_4C_6H_5)$.—This was obtained by oxidizing the benzoin by means of copper sulfate in dilute pyridine. The yield of the diketone was 95%. The diphenylbenzil is very soluble in hot benzene and glacial acetic acid, but only slightly soluble in the cold solvents; light yellow needles, m. p. 141–142°. The quinoxaline, cream-colored iridescent needles, melts at 209–210°.

Anal. (of the benzil). Calcd. for $C_{26}H_{18}O_2$: C, 86.19; H, 4.97. Found: C, 86.03; H, 5.04. *Mol. wt.*, calcd.: 362. Found: 374.

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[10] Stolle, *Rer.*, 45, 281 (1912).

[11] Schlenk and Bergmann, *Ann.*, **463,** 20 (1928).

[12] *Cf.* Schonberg and Keller, *Ber.*, 56, 1638 (1923).

In order to verify further the structure of our benzil, the latter was allowed to react with an excess of phenylmagnesium bromide, and *p,p'*-diphenylbenzopinacol was obtained; m. p., 197–199°.[13]

Reduction by Magnesium Iodide and Magnesium.—The loss in weight of magnesium was 99.2% of the theoretical. On hydrolysis of the glycolate, the corresponding benzoin was obtained in a yield of 88%, and was identical with the product obtained from *p*-phenylbenzaldehyde by means of the benzoin condensation.

The reaction between the iodomagnesium glycolate and iodine attained equilibrium when 47% of the theoretical amount of the halogen had reacted. By the action of dried air on a solution of the glycolate, the polymer of the diphenylbenzilic acid anhydride was formed to the extent of 35%. This polymer, decomposition point 250°, was hydrolyzed with difficulty by hot aqueous potassium hydroxide, ultimately yielding the corresponding *p,p'*-diphenylbenzilic acid, m. p., 185–188°; Schlenk reports 178–181°.[14] The polymer, like the acid, produces a brilliant green color with concentrated sulfuric acid.

p,p'-Diphenylstilbene-diol-dibenzoate.—Benzoyl chloride reacts vigorously with glycolate. The dibenzoate so formed behaves as though it were composed of a mixture of the two possible stereoisomers, *cis* and *trans;* when heated it passes through two points of fusion, 180 and 203°, with intermediate solidification. If this mixture of the isomers is fused by heating to 210° and then recrystallized from benzene, the colorless needles obtained melt sharply at 200–203°, indicating the presence of the more stable isomer alone. The lower-melting isomer could not be isolated in the pure state.

Reduction with Magnesium Iodide Alone.—In the case of this benzil, also, we obtained free iodine from the reaction between the benzil and magnesium iodide. Equilibrium was reached when about one-third of the benzil had been transformed to the glycolate.

Reduction of p-Phenylbenzil

p-Phenylbenzil, $(C_6H_5C_6H_4)COCO(C_6H_5)$.—This unsymmetrical benzil was prepared by the oxidation of benzyl-p-biphenyl ketone[15] in the cold with potassium permanganate in aqueous pyridine solution, with a yield of 64%. After recrystallization from hot alcohol the light yellow plates melted at 105°.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.92; H, 4.90. Found: *C,* 84.17; H, 5.05. ***Mol. wt.,*** calcd.: 286. Found: 293.

The structure of this benzil was further verified by its rearrangement to *p*-phenylbenzilic acid, which Schlenk[14] had prepared in another manner.

Reduction by the Binary Systems.—In the reduction by $MgI_2 + Mg$, practically the theoretical amount of magnesium was used up, and an equivalent amount of magnesium hydroxide was formed on hydrolysis. From the benzene solution there was obtained a good yield of the *p*-phenylbenzoin, but with a rather low melting point. A more easily purified product was obtained on reduction by the system $MgBr_2 + Mg$; the originally transparent yellow solution became deep brown, then finally orange. The crude benzoin, recrystallized from hot alcohol, was obtained as a pure white powder; m. p. 148–151°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.33; H, 5.56. Found: C, 83.39; H, 5.61. ***Mol.*** wt., calcd.: 288. Found: 297.

It has not been established which isomer of the two possible benzoins this compound actually is.

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[13] Ref. 6, p. 251.

[14] Schlenk and co-workers, ***Ber.,*** **47,** 489 (1914).

[15] Ferriss and Turner, J. *Chem. Soc.,* **117,** 1148 (1920).

Summary

The unsaturated halogeno-magnesium glycolates obtained by reduction of various aromatic diketones have been prepared and their reactions studied. Several new benzils and benzoins necessary for this work have been prepared and described.

It has been found that magnesium iodide alone, even in the absence of metallic magnesium, has a decided reducing action on the diketone; the amount of glycolate formed is dependent upon the equilibrium: diketone $+ \mathrm{MgI_2} \rightleftharpoons$ glycolate $+ \mathrm{I_2}$. The amount of iodine thus set free is from 16 to 50% of the theoretical.

The characteristic color changes during and at the end of the reduction process suggest the probability of the existence in the unsaturated glycolates of molecules containing each two trivalent carbon atoms $\mathrm{R—(XMgO)}\underset{|}{\mathrm{C}}—\underset{|}{\mathrm{C}}\mathrm{(OMgX)R}$.

ANN ARBOR, MICHIGAN

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

THE SYNTHESIS OF SOME ALKYLXANTHINES[1,2]

BY D. W. MACCORQUODALE

RECEIVED APRIL 1, 1929 PUBLISHED JULY 5.1929

In view of the valuable therapeutic properties of the naturally occurring xanthine bases theophylline, theobromine and caffeine, it seems desirable that a study be made of the relation between the pharmacological action and the nature of the alkyl groups attached to the xanthine nucleus. This work was undertaken at the suggestion of the late Dr. A. S. Loevenhart in order to make available some of the homologs of these alkaloids for such a study.

A consideration of the various syntheses devised for the preparation of compounds of this type finally led to the selection of a series of reactions worked out by Emil Pischer during his researches on the purines and used by him for the preparation of caffeine.

Potassium urate when heated with phosphorus oxychloride yields 8-hydroxy-2,6-dichloropurine (I) which in turn is converted into trichloropurine when heated with a large excess of the same reagent.

The chlorine atom at position eight being much more firmly attached than those in the other positions, does not react with sodium ethoxide,

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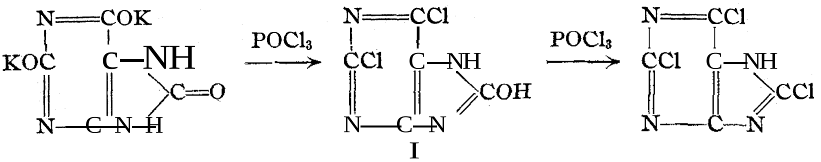
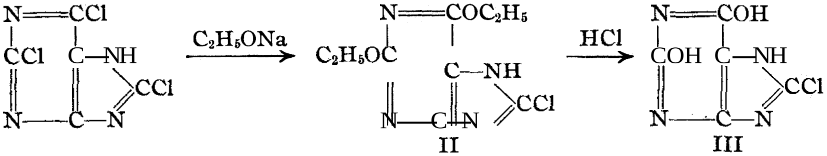
[1] This paper is constructed from a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Read before the Regional Meeting of the American Chemical Society at Minneapolis on June 19, 1928.



while the others are readily replaced by ethoxyl groups forming 2,6-diethoxy-8-chloropurine (II). The ethoxyl groups are easily replaced by hydroxyl groups by heating the compound with concentrated hydrochloric acid.



The 8-chloroxanthine (III) thus obtained is dissolved in aqueous potassium hydroxide solution and heated with two moles of alkyl iodide to form the 3,7-dialkyl-8-chloroxanthine, which can be reduced to the 3,7-dialkylxanthine or can be further alkylated to the 1,3,7-trialkyl-8-chloroxanthine, which upon reduction yields the 1,3,7-trialkylxanthine. It was found that the 1,3,7-trialkyl-8-chloroxanthine cannot be readily obtained in one operation from the 8-chloroxanthine, for even when a considerable excess of the alkylating agents is used the yield of trialkylchloroxanthine is small and the yield of dialkylchloroxanthine relatively large. This is in agreement with the work of Biltz and Peukert,[3] who found that the ethylation of 3-ethyl-8-chloroxanthine produced 3,7-diethyl-8-chloroxanthine, but they did not attempt to ethylate this compound further. Other evidence to show that xanthine and its substitution products are most readily alkylated in the 3- and 7-positions is found in the work of Fischer, who showed that theobromine is formed by the methylation of xanthine,[4] that the methylation of 3-methylxanthine also produces theobromine[5] and that chlorotheobromine can be obtained by the methylation of 3-methyl-8-chloroxanthine.[6]

By the ethylation of 8-chloroxanthine (III) a compound was obtained which analysis showed to be a diethylchloroxanthine. That it was the 3,7-isomer which would be expected was shown by its reduction to 3,7-diethylxanthine,[3] but its melting point (207°) did not agree with that of the 3,7-diethyl-8-chloroxanthine obtained by Biltz and Peukert, who give its melting point as 238°. They proved the structure of their compound by hydrolyzing it with alkali and obtaining 3,7-diethyluric acid,

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[3] Biltz and Peukert, Ber., 58,2198 (1925).

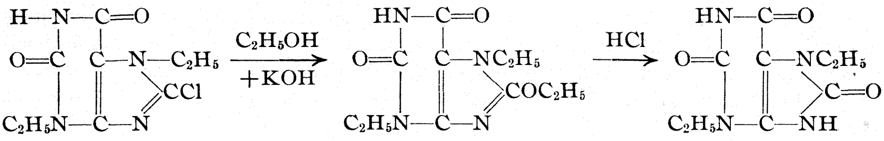
[4] Fischer, Ann., 215,311 (1882).

[5] Fischer and Ach, Ber., 31, 1987 (1898).

[6] Ref. 5, p. 1984.

which had previously been prepared by Biltz and Sedlatschek.[7] We attempted to hydrolyze our compound both by boiling with normal potassium hydroxide solution and by heating to 125–130° with concentrated hydrochloric acid for five hours; in both cases the substance was recovered unchanged.

The diethylchloroxanthine was finally converted into 3,7-diethyluric acid (IV) by treatment with potassium hydroxide in absolute alcohol solution. 3,7-Diethyl-8-ethoxyxanthine was thus obtained and this compound; upon heating with concentrated hydrochloric acid, readily yielded the 3,7-diethyluric acid prepared by Biltz and Sedlatschek.



IV

Contrary to statements of these authors it was found that this compound suffers decomposition at its melting point and so it proved unsuited for identification of the diethylchloroxanthine. This was accomplished, however, by methylation of the diethyl-8-chloroxanthine, treatment of the methyldiethyl-8-chloroxanthine with alcoholic potassium hydroxide to form methyldiethyl-8-ethoxyxanthine, and hydrolysis of this with concentrated hydrochloric acid to form a compound identical with the 1-methyl-3,7-diethyluric acid of Biltz and Sedlatschek,[7] thus proving the structure of the 3,7-diethyl-8-chloroxanthine, and also of each of the intermediate compounds.

By application of these methods the ethyl and normal butyl analogs of theobromine and caffeine were obtained as well as a number of other new purine derivatives.

Experimental Part

2,6-Dichloro-8-hydroxypurine.—This was prepared by Fischer's[8] method, the yields varying from 42 to 48% of the theoretical. It was partly purified by boiling with three times its weight of concentrated nitric acid, further purification being found unnecessary for the preparation of trichloropurine.

Trichloropurine.—This was prepared as described by Fischer[9] and yields of 46 to 50% of the theoretical were obtained.

2,6-Diethoxy-8-chloropurine.—The method described by Fischer[10] was followed except that it was found unnecessary to heat the reactants in a sealed vessel. The reaction takes place readily when a hot solution of trichloropurine in absolute alcohol is added slowly to a boiling alcoholic solution of sodium ethoxide under a reflux condenser; yield, 64–73% of the theoretical.

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[7] Biltz and Sedlatschek, *Ber.*, 57, 179 (1924).

[8] Fischer and Ach, *ibid.*, 30, 2209 (1897).

[9] Fischer, *ibid.*, 30, 2221 (1897).

[10] Fischer, *ibid.*, 30, 2234 (1897).

8-Chloroxanthine.—This was prepared exactly as described by Fischer,[10] the yield of crude product being 91% of the theoretical. It was purified by crystallization of the ammonium salt from dilute ammonia solution and subsequent decomposition of the salt with hydrochloric acid.

3,7-Diethyl-8-chloroxanthine.—Five grams of 8-chloroxanthine was dissolved in 68.5 cc. (2.25 molecular equivalents) of 0.917 *N* potassium hydroxide solution and shaken in a closed vessel with 9.4 g. (2.25 molecular equivalents) of pure ethyl iodide for one and one-half hours at 90–95". The light yellow, crystalline product was filtered off, washed with water and then treated with very dilute potassium hydroxide solution whereupon it readily passed into solution, leaving practically no residue. In the cases of those runs in which larger proportions of alkali and ethyl iodide were used a small amount of alkali-insoluble material was obtained which proved to be triethylchloroxanthine but its amount was never very great. Upon addition of a slight excess of dilute hydrochloric acid to the filtrate the product was precipitated as a white crystalline solid which was filtered off, washed with cold water and dried at 110°. The yield was 1.6–2.0 g. For the analysis it was crystallized from a large volume of hot water and dried at 110°.

Anal. Calcd. for $C_9H_{11}O_2N_4Cl$: Cl, 14.62. Found: Cl, 14.40, 14.23.

The compound dissolves in hot alcohol, benzene, ethyl acetate and acetone, and separates in white needles on cooling. It is very soluble in chloroform. It is difficultly soluble in hot water and the solution on cooling deposits beautiful white needles. After one such crystallization the substance melted at 201–202° (207° corrected) and a recrystallization did not raise the melting point. Biltz and Peukert give the melting point of this substance as 238° but this is evidently a typographical error and probably 208" is intended. Upon reduction with hydriodic acid and phosphonium iodide it yields 3,7-diethylxanthine melting at 183°.

3,7-Diethyl-8-ethoxyxanthine.—One gram of 3,7-diethyl-8-chloroxanthine was heated for two hours under reflux with 15 cc. of a 10% solution of potassium hydroxide in absolute alcohol. A precipitate of potassium chloride began to separate soon after the heating was started. The alcoholic solution was evaporated to about 3 cc. and then was diluted with 20 cc. of water. The solution was acidified with hydrochloric acid and the voluminous white precipitate filtered off, washed with water and dried at 110°; yield, 0.93 g. After being recrystallized from alcohol the melting point was 207° (212° corrected). The analysis for nitrogen was by the Kjeldahl method.

Anal. Calcd. for $C_{11}H_{16}O_3N_4$: N, 22.22. Found: N, 22.12, 22.39.

The 3,7-diethyl-8-ethoxyxanthine is easily soluble in benzene, chloroform, acetone and glacial acetic acid. It dissolves sparingly in ether. Strong acids and dilute alkali solutions dissolve it easily. In hot water it dissolves only very slightly and separates again on cooling in fine, short, white needles. It is readily soluble in hot alcohol–water mixtures and these solutions on cooling deposit long, closely matted, hair-like needles.

3,7-Diethyluric Acid.—One tenth of a gram of 3,7-diethyl-8-ethoxyxanthine was dissolved in 2 cc. of concentrated hydrochloric acid (sp. gr. 1.19) and heated on the water-bath for twenty minutes. White crystals began to separate from the clear solution almost immediately. A little water was added and after the mixture had been cooled to 5° the product was filtered off and washed with a little cold water. The crystals were dissolved in 5 cc. of hot water to which had been added a drop of concentrated hydrochloric acid and 2 cc. of 95% alcohol. The solution was filtered and upon cooling and standing the diethyluric acid separated in small white crystals which were filtered off, washed with water and dried in the oven at 110°. The melting point was 360–365° (371–376° corrected) with decomposition. Biltz and Sedlatschek give the melting point as 350–355° without decomposition.

1-Methyl-3,7-diethyl-8-chloroxanthine.—Two grams of 3,7-diethyl-8-chloroxanthine was dissolved in 100 cc. of 0.917 N potassium hydroxide solution and 2 g. (excess) of pure methyl iodide was added. This was sealed in a pyrex bomb tube and shaken at 80–85° for two and one-half hours. When cool the crystalline product was filtered off and washed with very dilute potassium hydroxide solution to remove any unchanged diethylchloroxanthine and free iodine. After washing with water and drying at 105° it weighed 1.78 g. For the analysis it was recrystallized from 50% alcohol, from which it separated in beautiful white needles which melted at 113° (114.5° corrected).

Anal. Calcd. for $C_{10}H_{13}O_2N_4Cl$: Cl, 13.82. Found: Cl, 13.97, 13.73.

The compound is insoluble in water and in alkali but dissolves readily in strong hydrochloric acid. It dissolves in acetone, chloroform, benzene, ether and glacial acetic acid.

1-Methyl-3,7-diethyl-8-ethoxyxanthine.—Seven-tenths of a gram of 1-methyl-3,7-diethyl-8-chloroxanthine was heated under a reflux condenser with a 10% solution of potassium hydroxide in absolute alcohol for forty minutes. Potassium chloride separated rapidly during the heating. Most of the alcohol was removed by evaporation and the solution was acidified with dilute acetic acid. The voluminous white product was filtered off, washed with water and dried; yield 0.43 g. It was recrystallized from 50% alcohol; m. p. 111° (112° corrected).

Anal. Calcd. for $C_{12}H_{18}O_3N_4$: N, 21.05. Found: N, 20.68.

The compound is insoluble in water and in alkali but dissolves readily in strong hydrochloric acid. It is readily soluble in alcohol, ether, benzene, acetone and chloroform.

1-Methyl-3,7-diethyluric Acid.—Fifty milligrams of 1-methyl-3,7-diethyl-8-ethoxyxanthine was dissolved in 3 cc. of concentrated hydrochloric acid and heated on the water-bath for fifteen minutes, the solution being allowed to evaporate to dryness at the end of this period. The white crystalline residue was dissolved in 1.5 cc. of boiling 95% alcohol and chilled to −10°. The white crystalline product was filtered off and washed with a few drops of alcohol. It melted sharply without decomposition at 258° (266° corrected). Biltz and Sedlatschek obtained this compound by heating 1-methyl-3,7,9-triethyluric acid with hydrochloric acid and found it to have a melting point of 257–258°.

1,3,7-Triethyl-8-chloroxanthine.—Four grams of 3,7-diethyl-8-chloroxanthine was dissolved in 18.4 cc. of 0.895 N potassium hydroxide and 5.0 g. of pure ethyl iodide added. The mixture was shaken in a closed vessel at 90–95° for two hours. The solid product was filtered off and leached with very dilute potassium hydroxide solution and then washed with water. The air-dried product weighed 2.05 g. Upon acidification of the potassium hydroxide solution with hydrochloric acid, 0.48 g. of unchanged diethylchloroxanthine was obtained. The product was recrystallized from 50% alcohol; m. p. 79–80°.

Anal. Calcd. for $C_{11}H_{15}O_2N_4Cl$: Cl, 13.10. Found: Cl, 12.89, 12.81.

The triethyl-8-chloroxanthine is insoluble in water and alkali but dissolves readily in hydrochloric acid. It is also soluble in alcohol, ether, acetone, benzene, chloroform and glacial acetic acid.

1,3,7-Triethylxanthine.—Four grams of pure 1,3,7-triethyl-8-chloroxanthine was dissolved in 20 cc. of fuming hydriodic acid (sp. gr. 1.96) and heated on the water-bath with the occasional addition of small amounts of finely pulverized phosphonium iodide. When iodine was no longer liberated the reduction was over. This required about eight hours. The solution was evaporated on the water-bath until only a thick paste of crystals of the hydriodide of triethylxanthine remained. The crystals were dissolved in 15 cc. of water and dilute ammonium hydroxide solution added to liberate the base. The solution was chilled and the white crystalline product filtered off, washed and dried in the air; wt. 3.05 g. From the mother liquor a small crop of crystals was obtained upon concentration. The compound was purified by recrystallization from dilute alcohol; m. p. 113°.

Triethylxanthine was first obtained by Scarlat[11] by means of Traube's synthesis. He gives the melting point as 115°. Like caffeine it has no acid properties but acts as a weak base. It is difficultly solpble in water but dissolves readily in strong hydrochloric acid. It also dissolves in alcohol, ether, acetone, benzene, chloroform and glacial acetic acid. It can be volatilized undecomposed at atmospheric pressure.

3,7-Dibutyl-8-chloroxanthine.—The butylation of 8-chloroxanthine was found to proceed in exactly the same manner as the ethylation, that is, upon shaking the chloroxanthine with an excess of alkali and butyl iodide at 130°, the main product obtained was a dibutylchloroxanthine, only a very small amount of the tributyl derivative being formed. For the preparation of 3,7-dibutyl-8-chloroxanthine, 10.0 g. of 8-chloroxanthine was dissolved in 126 cc. of 0.895 N potassium hydroxide and 20.8 g. of pure *n*-butyl iodide was added. This was shaken in a closed vessel for two hours at 130°. The solid product was filtered from the well-cooled reaction mixture and purified in the manner described for 3,7-diethyl-8-chloroxanthine. The yield of crude product was 7.9 g. After recrystallization from 60% alcohol the melting point was 142.5 (145° corrected).

Anal. Calcd. for $C_{13}H_{19}O_2N_4Cl$: Cl, 11.87. Found: Cl, 11.86.

The 3,7-dibutyl-8-chloroxanthine is very slightly soluble in boiling water and separates in crystals on cooling. It dissolves readily in dilute alkali and in strong hydrochloric acid. It is readily soluble in alcohol, acetone, benzene, chloroform and glacial acetic acid, and somewhat less readily soluble in ether.

3,7-Dibutylxanthine.—This was prepared by the reduction of 3,7-dibutyl-8-chloroxanthine in a manner precisely the same as that described for the preparation of triethylxanthine. From 1 g. of 3,7-dibutyl-8-chloroxanthine 0.83 g. of dibutylxanthine was obtained which after recrystallization from dilute alcohol had a melting point of 124–125° (127° corrected).

Anal. Calcd. for $C_{13}H_{20}O_2N_4$: N, 21.20. Found: N, 21.11, 21.24.

The 3,7-dibutylxanthine is very sparingly soluble in boiling water, from which it crystallizes on cooling. Dilute alkali and strong hydrochloric acid dissolve it readily. It dissolves with ease in alcohol, acetone, benzene, chloroform and glacial acetic acid, and a little less readily in ether.

1,3,7-Tributyl-8-chloroxanthine.—Six grams of 3,7-dibutyl-8-chloroxanthine was dissolved in 28.2 cc. (25% excess) of 0.895 N potassium hydroxide solution and 4.7 g. (25% excess) of pure n-butyl iodide added. The mixture was shaken in a closed vessel at 125–130° for two hours. When the vessel was allowed to cool the product remained as a viscous brown oil. The reaction mixture was shaken with 20 cc. of pure redistilled benzene to dissolve the oil and the benzene solution was shaken three times with 5% potassium hydroxide solution. From this alkaline solution there was recovered 0.4 g. of dibutylchloroxanthine by acidification with dilute hydrochloric acid. The benzene solution was washed three times with water and then dried over anhydrous sodium sulfate. The benzene solution was filtered into a small distilling flask and the solvent distilled off, the last traces being removed at 10-mm. pressure and the temperature of the boiling water-bath. The flask was then heated strongly, the pressure being maintained at 10 mm., and the product began to distil at 232° (uncorrected), about 80%

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[11] Scarlat, Bull. Sciences *Bucarest,* 13, 155–159 (1903).

of it distilling before the temperature reached 240°. The distillate was light yellow in color and weighed 4.2 g.

Anal. Calcd. for $C_{17}H_{27}O_2N_4Cl$: Cl, 9.99. Found: Cl, 9.92, 9.98.

The 1,3,7-tributyl-8-chloroxanthine is a viscous oil, soluble in alcohol, ether and benzene. An unsuccessful attempt was made to form the hydrochloride salt by precipitation from dry ether and benzene solutions with dry hydrogen chloride.

1,3,7-Tributylxanthine.—This compound, which is the butyl analog of caffeine, was prepared by the reduction of 1,3,7-tributyl-8-chloroxanthine with fuming hydriodic acid and phosphonium iodide in the manner already described. The free base was obtained as a colorless oil which solidified when chilled with ice and salt. It was filtered off and washed with water, and after drying thoroughly was dissolved in 155 cc. of absolute alcohol and the solution was saturated with dry hydrogen chloride gas. Then 30 cc. of dry ether was added and the solution cooled to 0° whereupon the hydrochloride of tributylxanthine separated almost completely in white crystals which were filtered off and washed with dry ether. The yield was 2.20 g. from 3.30 g. of tributylchloroxanthine. The salt was recrystallized from an alcohol—ether solution (1:2) saturated with hydrogen chloride and after being washed with dry ether was dried in a vacuum desiccator over calcium chloride and solid caustic potash. The melting point was 131–134°.

Anal. Calcd. for $C_{17}H_{29}O_2N_4Cl$: Cl, 9.94. Found: Cl, 9.75, 9.51.

The free base was liberated from the salt by dissolving the latter in a few cc. of 95% alcohol and adding dilute ammonium hydroxide solution. Upon chilling the solution in ice and salt the tributylxanthine separated as a colorless oil which gradually crystallized and was filtered off and washed with dilute alcohol. It was recrystallized again from alcohol, being obtained as pure white crystals which melted at 4142°.

Anal. Calcd. for $C_{17}H_{28}O_2N_4$: N, 17.56. Found: N, 17.56.

The 1,3,7-tributylxanthine is a white crystalline solid which is practically insoluble in water and alkali. It dissolves readily in strong acids, forming salts which are hydrolyzed upon dilution. It can be volatilized at atmospheric pressure without decomposition. It dissolves easily in the common organic solvents such as alcohol, ether, acetone, benzene, chloroform and glacial acetic acid.

To Dr. Homer Adkins, under whose supervision this work was carried out, the author wishes to express his thanks for many valuable suggestions made during the course of this investigation.

Summary

1. The ethyl and the n-butyl analogs of caffeine and theobromine have been prepared, the latter for the first time and the former by a method not heretofore used for the preparation of these compounds.

2. A number of other new derivatives of xanthine have been synthesized and described.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE FORCED REACTION OF PHENYL ISOCYANATE, PHENYL ISOTHIOCYANATE AND BENZOPHENONE-ANIL WITH PHENYLMAGNESIUM BROMIDE. AN UNUSUAL TYPE OF 1,4-ADDITION TO A CONJUGATED SYSTEM THAT IS PART ALIPHATIC AND PART AROMATIC

BY HENRY GILMAN, J. E. KIRBY AND C. R. KINNEY

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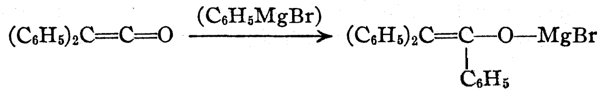
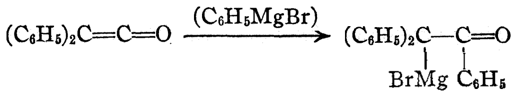
Introduction

In a study of compounds having terminal cumulated unsaturated groups, Gilman and Heckert[1] showed that phenylmagnesium bromide added to diphenylketene in the following manner



$$(C_6H_5)_2C{=}C{=}O \xrightarrow{(C_6H_5MgBr)} (C_6H_5)_2C{=}\underset{C_6H_5}{\underset{|}{C}}{-}O{-}MgBr \qquad (I)$$

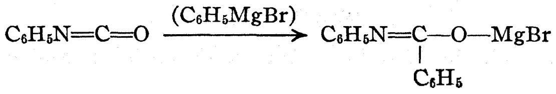
and not as follows



$$(C_6H_5)_2C{=}C{=}O \xrightarrow{(C_6H_5MgBr)} (C_6H_5)_2\underset{BrMg}{\underset{|}{C}}{-}\underset{C_6H_5}{\underset{|}{C}}{=}O \qquad (II)$$

The mode of addition represented by Reaction II is that which was currently in vogue at that time, inasmuch as the addition reactions of ketenes were then assumed to take place through a preliminary addition to the ethylenic linkage. Subsequently the earlier explanations for many addition reactions were altered to conform with that mechanism which postulates prior addition to the carbonyl group.[2]

Because of the marked similarity in many respects between ketenes and isocyanates, it might have been predicted that phenylmagnesium bromide would add to the terminal —C=O group and not to the —N=C group of phenyl isocyanate, in the following manner



$$C_6H_5N{=}C{=}O \xrightarrow{(C_6H_5MgBr)} C_6H_5N{=}\underset{C_6H_5}{\underset{|}{C}}{-}O{-}MgBr \qquad (III)$$

This reaction was studied by Gilman and Kinney[3] and although they did not get unequivocal proof for the type of addition postulated in Reaction III, they did show that addition could not have taken place at the —N=C linkage. By analogy with the reaction of the related phenylisothiocyanate, $C_6H_5N{=}C{=}S$, and by the established relative inertness of the —OMgX grouping,[4] they showed that Reaction III was undoubtedly

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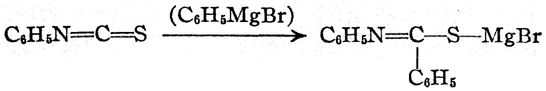
[1] Giman and Heckert, THIS JOURNAL, 42,1010 (1920).

[2] Staudinger, *Helv. Chim. Acta*, 5, 87 (1922).

[3] Gilman and Kinney, THIS JOURNAL, 46,493 (1924).

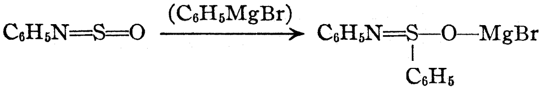
[4] Gilman and Schulze, *Rec. trav. chim.* 47,752 (1928).

correct. Gilman and Kinney[3] showed very definitely that phenylmagnesium bromide reacts with phenyl isothiocyanate as follows



$$C_6H_5N{=}C{=}S \xrightarrow{(C_6H_5MgBr)} C_6H_5N{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}S{-}MgBr \qquad \text{(IV)}$$

Subsequently Gilman and Morris[5] showed that the following reaction very probably occurs between phenylmagnesium bromide and thionylaniline



$$C_6H_5N{=}S{=}O \xrightarrow{(C_6H_5MgBr)} C_6H_5N{=}\underset{\displaystyle C_6H_5}{\underset{|}{S}}{-}O{-}MgBr \qquad \text{(V)}$$

There are two marked similarities between these several reactions. First, in each case addition takes place at the ultimate unsaturated group of these types having terminal cumulated unsaturated groups. Second, the reaction stops at this unsaturated group even with a liberal excess of phenylmagnesium bromide and extended refluxing at the low temperatures given by ether as a medium. This is hardly unexpected with ketenes inasmuch as such subsequent addition would involve addition to an ethylenic linkage, and Gilman and co-workers[6] have made a good case for the non-addition of the Grignard reagent to an ethylenic linkage. We are not so certain of the —N═S group in thionylaniline, but if such a grouping has anything in common with a related —N═O group, then it is to be expected that the —N═S group should add phenylmagnesium bromide.[7]

We can speak with greater assurance and definiteness on the —N═C linkage in phenyl isocyanate and phenyl isothiocyanate. It is known that organomagnesium halides add to the —N═C— group. Accordingly, it is reasonable to expect when phenyl isocyanate (or phenyl isothiocyanate) is refluxed for an extended time and at elevated temperatures with an excess of phenylmagnesium bromide, that subsequent to addition to the terminal —C═O (or —C═S) group, a second molecule of Grignard reagent should add to the —N═C— linkage; this explains the primary objective of this paper.

When phenylisocyanate was refluxed in an ether–toluene mixture (70–80°) with a liberal excess (5 or 6 equivalents) of phenylmagnesium bromide for about eight hours, the chief product obtained (in yields

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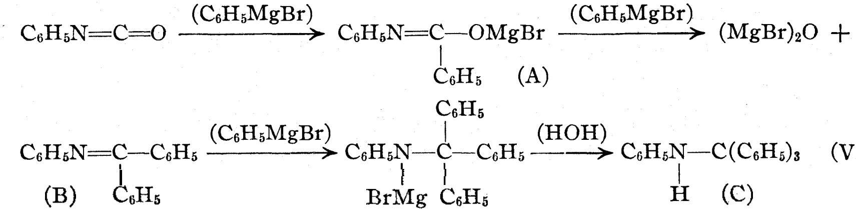
[5] Gilman and Morris, This Journal, 48,2399 (1926). See Footnote 6 in the paper by G. and M. on the reaction between RMgX compounds and aliphatic diazo compounds and diazo-imides.

[6] One of the more recent references to the non-addition of RMgX compounds to an ethylenic linkage is Gilman and McGlumphy, *Rec. trav. chim.*, 47, 418 (1928). This paper contains references to earlier studies.

[7] See Gilman and McCracken, This Journal, 49,1052 (1927), and 51,821 (1929), for the reaction of the Grignard reagent with nitroso and nitro compounds.

reaching 44%) was a compound melting at 144°. The ultimate analysis and molecular weight determination showed the compound to have a molecular formula agreeing with triphenylmethylaniline. It is easy to understand, from the following reactions, how triphenylmethylaniline might have formed



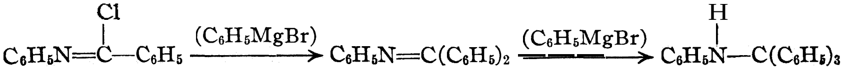
$$C_6H_5N{=}C{=}O \xrightarrow{(C_6H_5MgBr)} C_6H_5N{=}\underset{\substack{|\\ C_6H_5}}{C}{-}OMgBr\ \text{(A)} \xrightarrow{(C_6H_5MgBr)} (MgBr)_2O +$$

$$\text{(B)}\ C_6H_5N{=}\underset{\substack{|\\ C_6H_5}}{C}{-}C_6H_5 \xrightarrow{(C_6H_5MgBr)} C_6H_5\underset{\substack{|\\ BrMg}}{N}{-}\overset{\substack{C_6H_5\\ |}}{\underset{\substack{|\\ C_6H_5}}{C}}{-}C_6H_5 \xrightarrow{(HOH)} C_6H_5\underset{\substack{|\\ H}}{N}{-}C(C_6H_5)_3\ \text{(C)} \quad \text{(VI)}$$

The same product would result if prior to or simultaneous with replacement of the —OMgBr group by C_6H_5— the phenylmagnesium bromide had added to the —N=C— group in Compound (A).

The possible formation of triphenylmethylaniline, Compound (C), was rendered more reasonable when it was found that the 144° compound was obtained in equally high yields from the forced reaction not only with phenyl isocyanate but also with phenyl isothiocyanate and benzophenone-anil (Compound (B)). The formation of the same compound from the three different reactants proved that the terminal oxygen and sulfur, respectively, were replaced by two phenyl groups, and made it altogether reasonable that benzophenone-anil was an intermediate compound.

However, despite the fact that the melting point of our compound was near that of triphenylmethylaniline (147°) and that every reasonable prediction led to the expected formation of triphenylmethylaniline from the three compounds studied, the 144° compound certainly was not triphenylmethylaniline. Furthermore, the expected triphenylmethylaniline could not have been, in all probability, an intermediate. This was shown in an experiment in which triphenylmethylaniline was refluxed in an ether–toluene mixture for ten hours with five equivalents of phenylmagnesium bromide. Practically all of the triphenylmethylaniline was recovered unchanged. Our confusion was increased when we later found that Busch and Fleischmann[8a] obtained some triphenylmethylaniline from the reaction between benzanilideimidechloride and phenylmagnesium bromide. The formation of triphenylmethylaniline in their reaction is readily understandable[8b] from the following



$$C_6H_5N{=}\overset{\substack{Cl\\ |}}{C}{-}C_6H_5 \xrightarrow{(C_6H_5MgBr)} C_6H_5N{=}C(C_6H_5)_2 \xrightarrow{(C_6H_5MgBr)} C_6H_5\overset{\substack{H\\ |}}{N}{-}C(C_6H_5)_3 \quad \text{(VII)}$$

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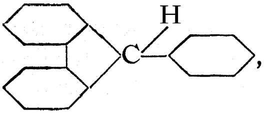
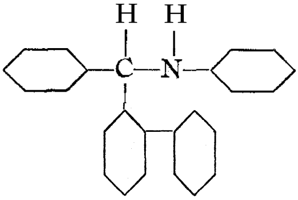
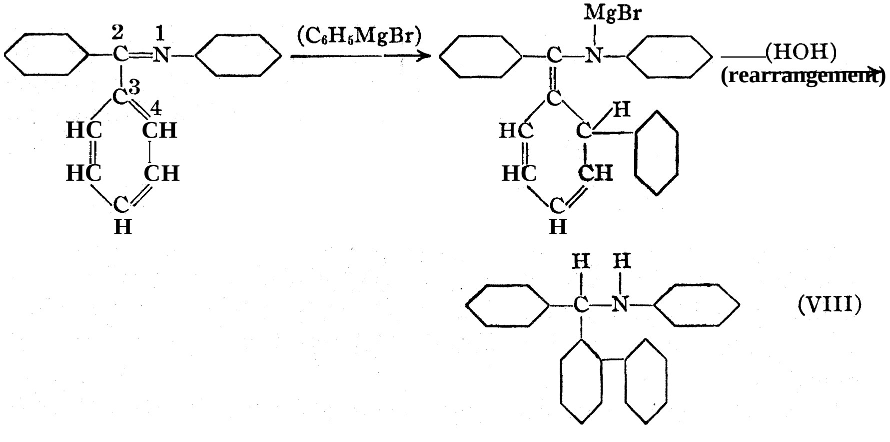
[8] (a) Busch and Fleischmann, *Ber.*, **43**, 2553 (1910). (b) The triphenylmethylaniline which they obtained might have come from reactions other than those illustrated in Reaction VII. For example, there may have been addition to the —N=C linkage prior to or simultaneous with replacement of the chlorine by a phenyl group.

It is interesting to recall their observation that they were unable to repeat this experiment. Also, their major reaction product was benzophenone-anil (Compound (B)). Although triphenylmethylaniline was not isolated in our several experiments, it would be unwise to say that it was not present, because the forced conditions of the reaction gave oily products which were not altogether tractable.

Triphenylmethylaniline hydrolyzes with ease to triphenylcarbinol and aniline. The 144° compound when hydrolyzed gave phenylfluorene, 

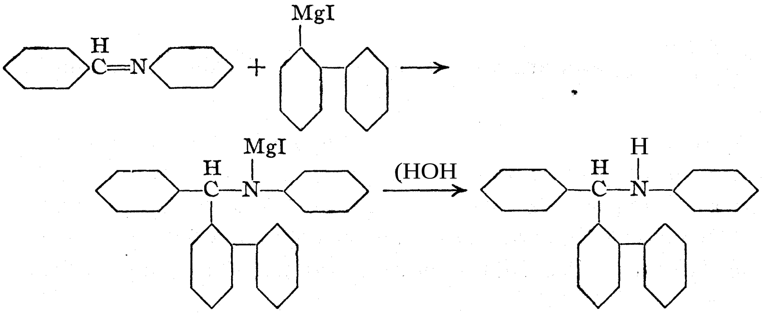
, and aniline. It was next shown that under our conditions of hydrolysis, triphenylcarbinol did not go over to phenylfluorene. The identification of phenylfluorene as a product of hydrolysis of the 144° compound was of help in suggesting several possible formulas for the 144° compound. Some critical experiments showed the impossibility of all but one of these formulas. We finally showed that the 144° compound must be *o*-**phenylbenzohydrylaniline,** 

. The idea for this compound came with the thought that inasmuch as addition of phenylmagnesium bromide probably did not take place at the —N=C— linkage (as evidenced by the absence of triphenylmethylaniline), 1,4-addition might have taken place with the conjugated system formed by the —N=C— group and **a** so-called ethylenic linkage in one of the phenyl groups attached to carbon, as follows



(VIII)

So far as we[7] know, a reaction of this type has not been reported with any class of compounds. A great deal of our present knowledge on the mode of 1,4-addition to conjugated systems rests on the excellent and thorough studies of Kohler and co-workers. Their studies were carried out, in the main, with organomagnesium halides. The rearrangement postulated in Reaction VIII may or may not be correct; that remains to be determined. However, there is no doubt concerning the structure of our o-phenylbenzohydrylaniline. It was synthesized as follows



(IX)

Over and against this method for the proof of structure of the *o*-phenylbenzohydrylaniline, a question may properly be raised on the choice of an anil (in this case, benzalaniline) in establishing the structure of a compound which was formed in a so-called abnormal manner from an anil (namely, benzophenone-anil). But benzophenone-anil is not benzalaniline, and we have shown that benzalaniline behaves normally even under forced conditions with phenylmagnesium bromide. Of course, there remains the possibility of abnormal reactions with *o*-biphenylmagnesium iodide. We know of no such abnormal reactions, but to remove all doubt the o-phenylbenzohydrylaniline should be synthesized by a reaction not involving RMgX compounds; this we propose to do.

Additional evidence is necessary for the support of Reactions VIII and IX. When the intermediate addition compound of the forced reaction between phenyl isocyanate and phenylmagnesium bromide, namely, Compound (D), is treated with diethyl sulfate, the —NMgBr grouping should be converted to an —NC_2H_5 grouping. Diethyl sulfate and related compounds have been shown to be eminently satisfactory reagents for the characterization of the —NMgX group? The product of this reaction with diethyl sulfate should be identical with that obtained from our o-phenylbenzohydrylaniline and diethyl sulfate. So far such identity is confined to the fact that the two products are oils, a fact which is without significance. However, the amines of this study have a marked tendency to form apparently intractable oils which crystallize slowly and with difficulty.

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[9] A leading reference is that of Gilman and Heck, This Journal, 50, 2223 (1928).

That the 144° compound contains a secondary amine grouping **is** shown by the Liebermann nitroso reaction for secondary amines, the Zerewitinoff method for active hydrogen and the formation of aniline as a product of hydrolysis.

As further indicative evidence for the correctness of Reaction VIII and, in particular, for Compound (D), we should state that the reaction mixture assumes a brilliant deep red color which fades appreciably on hydrolysis. This is what one might expect in view of the quinoid structure postulated for Compound (D).

If we grant the correctness of the reactions as postulated, there remains the desirability of proposing an explanation for this unusual type of 1,4-addition to a conjugated system. The most satisfactory explanation that we offer at this time involves the phenomenon of steric hindrance. We do so with full knowledge of the traditional weakness of such an explanation for some reactions. Quite recently Gilman and Heck[10] have shown that although some reactions of organomagnesium halides can be very satisfactorily explained on this basis, other reactions of a kind that might merit such an explanation cannot be correlated with the phenomenon of steric hindrance. From the studies reported at this time we know that one equivalent of phenylmagnesium bromide reacts very smoothly with phenyl isocyanate and phenyl isothiocyanate to give benzanilide and thiobenzanilide, respectively, and that the reaction apparently stops at this stage with an excess of phenylmagnesium bromide and extended refluxing in an *ether* solution.[3] We also know that benzophenone-anil reacts decidedly slowly, if at all, under the same conditions. This resistance to addition of phenylmagnesium bromide to this particular —N=C group (a resistance which we attribute at this time to steric influences) is so marked that when the reaction is forced at an elevated temperature, 1,4-addition takes place with the unique conjugated system designated in Reaction VIII.

It should be possible to find an answer to this question with subsequent studies on different anils and other related compounds with a variety of Grignard reagents and other compounds. Until at least several such studies have been completed it would be wise to defer suggestive theoretical considerations on the structure of benzene and the mechanism of substitution reactions of benzene.

The Experimental Part contains brief descriptions of some of the pertinent reactions carried out in connection with other possible structures that were considered prior to the identification of our 144° compound as *o*-phenylbenzohydrylaniline.

The authors wish to thank N. J. Beaber and A. P. Hewlett for some preliminary work and for valuable suggestions.

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[10] Gilman and Heck, *Ber.*, **62**, 1379 (1929).

Experimental Part

Preparation of o-Phenylbenzohydrylaniline from Phenylmagnesium Bromide. (1) Phenyl Isocyanate.—A vigorous reaction took place with the slow addition of **16** g. (**0.134** mole) of phenyl isocyanate in ether to **0.6** mole of phenylmagnesium bromide. When addition was complete, most of the ether was removed by distillation; toluene was added and the mixture was refluxed (internal temperature 70–80°) with stirring for six to eight hours. After hydrolysis by ice and hydrochloric acid, the ether–toluene layer was separated and steam distilled to remove toluene, diphenyl and other steam-distillable products. The non-volatile, sticky, reddish-brown paste that remained as a residue from the steam distillation was extracted with warm alcohol. The alcohol extractions on cooling usually deposited an oil. In some cases crystallization could be induced by rubbing with a glass stirring rod. When a little of the material solidified, it proved very effective in seeding other solutions. The compound was obtained as a yellowish powder melting between **139** and **142°**. It is sparingly soluble in alcohol, and a good solvent for crystallization is a mixture of **65%** alcohol and **35%** toluene. When recrystallized from this mixture, the compound is obtained as glistening yellow crystals melting at 143–144°. The yield from phenyl isocyanate was generally about 30%, but in some cases yields as high as 44% were obtained.

(2) Phenyl Isothiocyanate.—From **25.5** g. (**0.189** mole) of phenyl isothiocyanate and **0.8** mole of phenylmagnesium bromide refluxed for ten hours at 70–75° in an ether–toluene mixture, there was obtained **28.6** g. or a **45%** yield of the *o*-phenylbenzohydrylaniline. In the course of hydrolysis, hydrogen sulfide was evolved. The evolution of hydrogen sulfide is indicative of the formation of $(MgBr)_2S$ (or its equivalent) in accordance with Reaction VI.

(3) **Benzophenone-anil.**—From **19.3** g. (**0.075** mole) of benzophenone-anil and **0.3** mole of phenylmagnesium bromide refluxed for ten hours at 90–105° in an ether–toluene mixture, there was obtained **10.6** g. or a **42%** yield of the o-phenylbenzohydrylaniline. The reaction mixture prior to hydrolysis was deep purple in color. In some experiments hydrolysis was also effected by means of iced ammoniacal ammonium chloride.

Analysis and Properties of *o*-Phenylbenzohydryl-aniline.—Calcd. for $C_{25}H_{21}N$: C, **89.55**; H, **6.27**. Found: C, **89.38**, **89.75**; H, **6.87**, **6.53**. Mol. *wt.* Calcd., **335**. Found (in boiling acetone), **317**, **300** and **301**.

Hydrochloride.—The hydrochloride melting at 182.5° was obtained by adding hydrogen chloride to the amine dissolved in anhydrous ether. The free amine may be recovered from the salt by gently warming with dilute alcoholic potash. Analysis. Two samples of the hydrochloride were titrated with a standard solution of potassium hydroxide (and then back-titrated with a standard solution of hydrochloric acid). Calcd. molecular weight, **335**. Found: **337** and **335.9**.

Active Hydrogen by Zerewitinoff Analysis.—Two determinations by heating in xylene and amyl ether at 70° for fifteen minutes gave **0.7** and **0.69** active hydrogen. A third analysis under the same conditions with the exception of a fifty-minute period of heating at 70° gave **0.72** active hydrogen.[11] In these experiments the compound was dissolved in xylene and the methylmagnesium iodide was prepared in amyl ether. When, however, the determination was carried out with n-butyl ether as the solvent (both for the amine and the methylmagnesium iodide), the values obtained were **0.97** and **1.03** active hydrogen.[12]

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[11] Analyses by R. E. Fothergill.

[12] Analyses by R. J. VanderWal. It is interesting to note that triphenylmethylaniline in butyl ether reacts very slowly (eight hours at **70°** for completion) with methylmagnesium iodide in butyl ether to give **1.00** and **1.01** active hydrogen. This is one of a number of striking illustrations of what appear to be cases of steric hindrance. Others

With xylene as a solvent for the amine and n-butyl ether as a solvent for the Grignard reagent, the value was 0.75 active hydrogen.[12]

Splitting Reactions. (1) **Concd.** Hydrochloric Acid.—When 5 0 g. of the amine was heated in a sealed tube with 75 cc. of concd. hydrochloric acid for three hours at 145°, there were obtained 3.6 g. (a 99.6% yield) of 9-phenylfluorene and aniline. That triphenylcarbinol was not an intermediate product of this hydrolysis was shown by a parallel experiment in which triphenylcarbinol was heated under like conditions. The product in this case was triphenylmethane.

(2) Alcoholic Hydrochloric Acid.—9-Phenylfluorene was also obtained when 5 g. of the amine was refluxed for seventeen hours with a mixture of 150 cc. of 95% alcohol and 50 cc. of concd. hydrochloric acid. Under corresponding conditions triphenylmethylaniline gave triphenylmethane. **Also,** triphenylcarbinol when refluxed under corresponding conditions for twenty-four hours gave a 96.8% yield of triphenylmethane.

(3) Acetyl Chloride and Acetic Anhydride.—In an attempt to acetylate the amine by means of acetic anhydride, an apparently intractable tar was obtained. In a subsequent experiment 9-phenylfluorene was obtained after refluxing 5 g. of the amine with a mixture of 25 cc. of acetyl chloride and 50 cc. of acetic anhydride.

The identity of every solid described in this study was confirmed by a mixed melting point determination with an authentic specimen. Synthetic 9-phenylfluorene was prepared by two different methods: first, by refluxing 10 g. of triphenylchloromethane in benzene for five hours with one g. of mossy zinc; and, second, by heating triphenylcarbinol with sirupy (85%) phosphoric acid.[13]

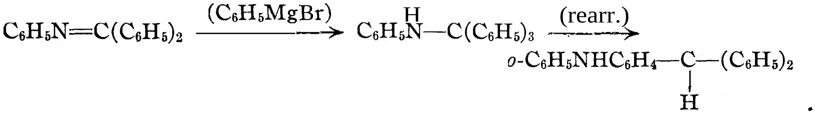
Miscellaneous.—The amine (3.9 g.) was recovered unaltered after refluxing for twelve hours in xylene. Its hydrochloride, when dry distilled, underwent considerable decomposition but gave a small quantity of 9-phenylfluorene in the distillate.

When 2 g. of the amine was refluxed for several hours with benzoyl chloride and pyridine and then worked up in the customary manner it gave a nitrogen containing compound which melted at 155–156°. However, we had no success in hydrolyzing this as yet unidentified compound to benzoic acid and the amine by means of alcoholic potash.

After refluxing 5 g. of the amine for twenty hours with 100 cc. of 20% alcoholic potash. 4.5 g. of the amine was recovered unchanged.

The yellowish color of the amine obtained from phenyl isocyanate, phenyl isothiocyanate and benzophenone-anil suggested at one time that the amine might be quinoidal in nature. Accordingly, some reduction experiments were carried out. Neither sodium and alcohol nor zinc and glacial acetic acid appeared to affect the amine. It was not until the amine was finally synthesized from benzalaniline and o-biphenylmagnesium iodide that we discovered the amine to be without color, or rather of a grayish-white color.

It was believed, for a time, that the amine melting at 144° was o-phenylaminotriphenylmethane, formed possibly by the rearrangement of triphenylmethylaniline, as follows



$$C_6H_5N{=}C(C_6H_5)_2 \xrightarrow{(C_6H_5MgBr)} C_6H_5\overset{H}{N}{-}C(C_6H_5)_3 \xrightarrow{(rearr.)} o\text{-}C_6H_5NHC_6H_4{-}\underset{\underset{H}{|}}{C}{-}(C_6H_5)_2 \quad (X)$$

This prompted some oxidation experiments with the hope of converting the supposed

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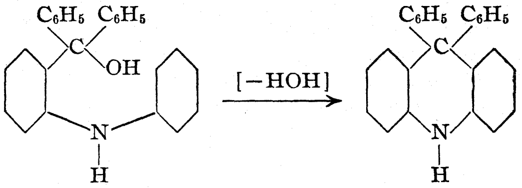
will be reported later by R. J. VanderWal. The values of triphenylmethylaniline in xylene are lower (0.81 and 0.92) after heating for fifteen hours at 70°.

[13] Kliegl, *Ber.,* 38, 287 (1905).

o-phenylaminotriphenylmethane to the known *o*-phenylaminotriphenylcarbinol, *o*-$C_6H_5NHC_6H_5—C(OH)—(C_6H_5)_2$. Mild treatment with nitric acid did not affect the amine, and gentle warming with nitric acid of sp. gr. 1.33 gave an intractable tar. Failing in this we thought we might achieve the same result by reducing the known *o*-phenylaminotriphenylcarbinol to o-phenylaminotriphenylmethane. However, we were equally unsuccessful in this, for when o-phenylaminotriphenylcarbinol was treated with alcohol and sulfuric acid,[14] formic acid,[15] glacial acetic acid and zinc dust or hydriodic acid and zinc dust, a sparingly soluble compound melting at 244–245° was obtained, and not our 144° amine. The 244–245° compound is the diphenyldihydroacridine of Baeyer and Villiger[16]


(XI)

Zinc dust and alkali, and catalytic reduction with the platinum catalyst of Adams were without effect on the o-phenylaminotriphenylcarbinol.

Triphenylmethylaniline and Phenylmagnesium Bromide.—After refluxing 5 g. (0.015 mole) of triphenylmethylaniline with 0.075 mole of phenylmagnesium bromide in an ether–toluene mixture at 100° for ten hours, 4 g. or 80% of the amine was recovered.

Benzalaniline and Phenylmagnesium Bromide.—A 48.5% yield of benzohydrylaniline, $(C_6H_5)_2CHNHC_6H_5$, was obtained after refluxing 18 g. (0.1 mole) of benzalaniline and 0.3 mole of phenylmagnesium bromide in an ether–toluene mixture for eight hours. No other product was isolated. In a comparable experiment with 14 g. (0.077 mole) of benzaniline, 0.1 mole of phenylmagnesium bromide and refluxing at 106° for eleven hours, the yield of benzohydrylaniline was 65%. This amine was identified as the hydrochloride melting at 194–195° and the nitrate melting at 158.5°.[17]

Some orienting experiments with benzanilide, $C_6H_5NHCOC_6H_5$, benzophenone-oxime, $(C_6H_5)_2C{=}NOH$, and benzophenone-oxime-o-methyl ether, $(C_6H_5)_2C{=}NOCH_3$, with phenylmagnesium bromide under forced conditions have not as yet yielded any of the expected o-phenylbenzohydrylaniline. The high recovery (69%) of benzophenone-oxime methyl ether might have been predicted from related experiments of Busch and Hobein[18] with oxime-ethers.

Preparation of o-Biphenylmagnesium Iodide.—The 2-nitrodiphenyl was prepared according to the directions of Bell, Kenyon and Robinson,[19] and then reduced to 2-aminodiphenyl by the method of Scarborough and Waters.[20]

Forty-three and one-half g. (0.21 mole) of 2-aminodiphenvl hydrochloride was diazotized in iced dilute hydrochloric acid by means of a solution of 14.5-g. (0.21 mole) of sodium nitrite. Then 100 g. of potassium iodide in 150 cc. of water was added slowly with continuous stirring. A heavy paste separated and after standing for

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[14] Schmidlin and Banùs, *Ber.*, 45, 3188 (1912).

[15] Kaufmann and Pannwitz, *ibid.*, 45, 769 (1912).

[16] Baeyer and Villiger, *ibid.*, 37, 3202 (1904).

[17] Bigelow and Eatnough, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 22.

[18] Busch and Hobein, *Ber.*, 40, 2097 (1907).

[19] Bell, Kenyon and Robinson, *J. Chem. Soc.*, 1239 (1926).

[20] Scarborough and Waters, *ibid.*, 89, (1927).

one and one-half hours the mixture was warmed gently to expel nitrogen; a few crystals of sodium thiosulfate were added to remove free iodine and the almost black oil was extracted with toluene. The toluene solution was washed with water, dried over calcium chloride and then distilled in a vacuum. The yield of *o*-iododiphenyl boiling at 158° (6 mm.) was 30.4 g. or 51.7%; d_{25}^{25}, 1.6038. The iodide was strongly resistant to nitric acid decomposition in the Carius analysis.

Anal. Calcd. for $C_{12}H_9I$: I, 45.3. Found: I, 44.6.

There was no difficulty in getting a Grignard reagent from 21.1 g. of the o-iododiphenyl and 1.82 g. of magnesium turnings. The reaction was started with the activated $12^3/_4\%$ copper–magnesium alloy of Gilman, Peterson and Schulze.[21] The Grignard reagent gave the color test of Gilman and Schulze,[22] and when an aliquot was treated with carbon dioxide in the customary manner[z3] o-diphenylcarboxylic acid[2*] was obtained.

Preparation of *o*-Phenylbenzohydrylaniline from Benzalaniline and o-Biphenylmagnesium Iodide.—A toluene solution of 13.6 g. (0.075 mole) of benzalaniline was added to the 0.075 mole of Grignard reagent. Since there was no evidence of reaction the ether was partially replaced by toluene until the boiling point of the mixture was 95°. Immediately on increasing the reaction temperature, a deep red color set in. This was the only evidence of reaction, although refluxing was continued for eight hours. Occasional color tests[22] were made during the heating and in every case a deep green color was obtained. It was discovered on hydrolysis that this green color might not have been due to any unused Grignard reagent. After hydrolysis, about 0.5 g. of solid was removed by filtration from the deep red toluene layer. All of the hydrolysis mixture was steam distilled without separating the layers. The acid hydrolysis mixture immediately assumed a deep green color when steam was passed into it. Some benzaldehyde distilled over: this may have been due to unaltered benzalaniline. The residual heavy, deep green tar was taken up in 250 cc. of an alcohol–toluene mixture containing about 25% of toluene. On standing for three to four hours, crystals started to separate. After about twenty-four hours the crystals were filtered off and washed thrice with alcohol. The yield was 9 g. or 35.8% of o-phenylbenzohydrylaniline, and very probably more of the amine was formed as it is a compound that is affected (at least colorimetrically) by atmospheric exposure in a way to impede crystallization. The compound showed no depression in a mixed melting point determination with the amine obtained from phenyl isocyanate and phenylmagnesium bromide.

Summary

The forced reaction of phenyl isocyanate, phenyl isothiocyanate and benzophenone-anil with an excess of phenylmagnesium bromide gives o-phenylbenzohydrylaniline. The formation of this amine is unique in the sense that it undoubtedly takes place as a result of a 1,4-addition to the —C=N group in the side chain and one of the so-called ethylenic linkages in a benzene ring.

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[21] Gilman, Peterson and Schulze, *Rec. trav. china.*, 47, 19 (1928).

[22] Gilman and Schulze, THIS JOURNAL, 47, 2002 (1925); Bull. *soc. chim.*, 41, 479 (1927).

[23] Giman and Parker, THIS JOURNAL, 46, 2816 (1924).

[24] Schmitz, *Ann.*, 193, 115 (1878); Pictet and Ankersmit, *ibid.*, 266, 143 (1891).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SHARP AND DOHME]

AMINO ALCOHOLS. I. PHENYLPROPANOLAMINE AND PARA-TOLYLPROPANOLAMINE

BY WALTER H. HARTUNG AND J. C. MUNCH

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The encouraging results from the pharmacodynamic investigations of ephedrine, particularly those of Chen,[1] have stimulated the interest of chemists in this compound as well as in its homologs and analogs.[2]

Since Smith[3] isolated *nor-d-ψ*-ephedrine from ephedra species and in view of the fact that (3,4-dihydroxyphenol)-ethanolamine has in many respects a physiological activity not unlike that of (3-4-dihydroxyphenyl)-ethanolmethylamine, or adrenaline,[4] it appeared that arylalkanolamines of the general types $ArCHOHCHRNH_2$ merited further study and investigation.

Various methods are recorded for the synthesis of compounds of this class. Phenylethanolamine has been prepared in low yields by reducing o-amino-acetophenone[5] or mandelonitrile[6] with sodium amalgam; Alles claimed better results from phenylnitro-ethanol.[2c] Phenylpropanolamine has been made by reducing a-aminopropiophenone with sodium or its amalgam;? by reducing phenylnitro-ethanol with zinc dust and acetic acid;[8] from isonitrosopropiophenone by catalytic means with palladinized gum arabic, but from 5.7 g. of isonitroso ketone in a solution of 85 cc. of alcohol, 57 cc. of water and 7.1 cc. of 30% hydrochloric acid, only 1.4 g. of phenylpropanolamine was isolated.[9] A method of more general application was developed by Tiffeneau and Lévy[10] who used the scheme

$$C_6H_5CHOHCN\ (or\ C_6H_5CHOH{\cdot}CONH_2) \xrightarrow{RMgX} C_6H_5CHOHCOR \xrightarrow{H_2NOH}$$

$$C_6H_5CHOHC({=}NOH)R \xrightarrow{H_2} C_6H_5CHOHCHRNH_2$$

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[1] Chen, *J. Pharmacol.*, 28, 31 (1926).

[2] (a) Hyde, Browning and Adams, THIS JOURNAL, 50, 2287 (1928); (b) Tiffeneau, *J. pharm. chim.*, [8] *7*, 228 (1928); (c) Alles, *J. Pharmacol.*, 32, 121 (1927); (d) Manske and Johnson, THIS JOURNAL, 51, 580 (1929).

[3] Smith, *J. Chem. Soc.*, 125, 51 (1928).

[4] Oswald, "Chemische Konstitution und Pharmakologishe Wirkung," Borntraeger, Berlin, 1924, pp. 361–363; Schultz, *Hygienic Lab.* Bull., 55, 31 (1909); Hugounenq and Florence, "Principes de Pharmacodynamie," Masson et Cie., Paris, 1928, p. 175.

[5] Pictet and Gams, *Ber.*, 43, 2385 (1910); Mannich and Thiele, *Arch. Pharm.*, 253, 181 (1915).

[6] Hess and Uibrig, *Ber.*, 48, 1984 (1915).

[7] Calliesz, *Arch. Pharm.*, 250, 150 (1912); Eberhardt, *ibid.*, 255, 143 (1917).

[8] Nagai, U. S. Patent 1,356,877 [C. *A.* 15, 412 (1921)].

[9] Hunnius and Rabe, *Ber.*, 45, 2166 (1912).

[10] Tiffeneau and Lévy, *Bull. soc. chim.*, [4] *37*, 1247 (1925); *Compt. rend.*, 183, 969 (1926).

the reduction of the alcohol-oxime being accomplished by means of sodium. This is a valuable method and by means of it various phenylalkanolamines, up to and including phenylhexanolamine, were made. However, the ultimate yields were not very large.

In order to facilitate a more complete study of various arylalkanolamines, a search was first made for a more satisfactory method of making them, which centered itself on finding a suitable means for reducing isonitroso ketones, since the work of Slater[11] indicated that these intermediates could be prepared pure and in good yields. The process finally adopted has been described by one of us.[12] The isonitroso ketone was dissolved in absolute acohol containing three equivalents of hydrogen chloride and shaken with palladinized charcoal in an atmosphere of hydrogen until saturated, whereby the ketonic group was reduced to a secondary alcohol and the oximino to a primary amine; the product was isolated as its hydrochloride, practically pure and in very good yield, by removing the catalyst, concentrating the alcoholic solution and diluting with excess ether. In the absence of hydrogen chloride the reduction was incomplete and the product was not the desired amino alcohol. Two compounds, phenylpropanolamine and p-tolylpropanolamine, have been prepared in this manner; others are under way and will be reported later.

Phenylpropanolamine has been known, but p-tolylpropanolamine, isomeric with ephedrine, is new. Pharmacologically both compounds produce effects paralleling those of ephedrine; they exert as great an effect on the blood pressure of an anesthetized dog as does the natural alkaloid and are also effective when administered orally. Their mydriatic action was found to be greater than that of either ephedrine or phenylethanolamine. Phenylethanolamine has no action when given by mouth.'' Both compounds had a potentiating effect when epinephrine was subsequently administered; that is, the effect of epinephrine was greatly increased.

The toxicity of phenylpropanolamine and p-tolylpropanolamine compared with that of natural ephedrine and phenylethanolamine[14] given by Alles (ref. 2c) and Miller and Piness (ref. 13) is shown in the table.

It is seen that the phenyl derivative is less toxic and the tolyl more toxic than ephedrine. The pharmacological investigation is being continued and the results will be published later elsewhere.

Procedure

The isonitrosopropiophenone and *p*-tolyl-α-oximino-ethyl ketone were prepared from freshly distilled butyl nitrite and propiophenone and *p*-

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[11] Slater, J. *Chem. Soc.*, 117, 587 (1920).

[12] Hartung, THIS JOURNAL, 50, 3370 (1928).

[13] Miller and Piness, J. Am. Med. *Assocn.*, 91, 1033 (1928).

[14] Toxicity figures for ephedrine and phenylethanolamine given by Alles (ref. 2c) and Miller and Piness (ref. 13).

TABLE I

PHARMACOLOGICAL STUDIES

	Minimum lethal dose, mg./kg.			
	Rats, intraperitoneal	Dogs, intraperitoneal	Rabbits, intravenous	Guinea pig, subcutaneous
Phenylpropanolamine	175	Over 500	75	600
p-Tolylpropanolamine	50	Over 100	33	200
Ephedrine	...	......	50	350
Phenylethanolamine	...	......	30	1000

methylpropiophenone, respectively; these were reduced as described above. The pure amino alcohols did not reduce Fehling's solution but formed with it a crystalline precipitate.[15] The incompletely hydrogenated product, however, did reduce Fehling's solution, and this fact as well as the measure of the hydrogen absorbed could be used in determining the completeness of the catalytic reduction. This test is based on the observation that the oximino group is more easily reduced than the carbonyl, the remarks of Hunnius and Rabe to the contrary notwithstanding; and it is well established that in alkaline solution α-amino ketones are readily oxidized to pyrazine derivatives.[16] Thus amino-acetone, in ammonia solution, is oxidized by mercuric chloride to dimethylpyrazine;[17] *p*-methyl-α-amino-acetophenone to 2,5-di-*p*-tolylpyrazine;[18] and α-aminopropiophenone is oxidized with methyl iodide to 3,6-diphenyl-2,5-dimethylpyrazine.[19]

Deamination by means of nitrous acid resulted in the formation of the original aryl alkyl ketones, identified as their semicarbazones. This is in harmony with the findings of Tiffeneau and Lévy,[20] who treated bases of the type $ArCHOHCHRNH_2$ with nitrous acid and obtained ketones of the type $ArCOCH_2R$. However, a peculiarity observed in connection with these deaminations was that unless the resulting product was first distilled, no semicarbazone could be isolated.

Experimental

Propiophenone and *p*-tolylethyl ketone were prepared by the regular Friedel–Crafts reaction of propionyl chloride on benzene and toluene, respectively.

Isonitrosopropiophenone was prepared from propiophenone and butyl nitrite. Slater[11] used methyl nitrite, a gas; butyl nitrite, a liquid, was found more convenient. In a 1-liter 3-necked, round-bottomed flask, fitted with stirrer, reflux and delivery tube for hydrogen chloride, was placed a solution of 80 g. of propiophenone (0.6 mole) in 400 cc. of ether; hydrogen chloride was passed through the stirred solution at the rate of 2–3 bubbles per second, stirring and addition of acid being continued throughout the reaction; then freshly distilled butyl nitrite, b. p. 75–81°, was added through the

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[15] *Cf.* Chen, *J. Am. Pharm. Assocn.*, **18**, 110 (1929).

[16] Houben–Weyl, "Die Methoden der Organischen Chemie," 3d ed., Georg Thieme, Leipzig, 1923, Vol. III, p. 402.

[17] Gabriel and Pinkus, *Ber.*, **26**, 2206 (1893)

[18] Reudenburg, *ibid.*, **46**, 3555 (1913).

[19] Eberhardt, *Arch. Pharm.*, **258**, 107 (1920).

[20] Tiffeneau and Lévy, *Compt. rend.*, **183**, 970 (1926).

reflux condenser in 2–3-cc. portions until a total of 61.8 g. (0.6 mole) was added. After addition of the first portion the reaction mixture slowly became a yellow-brown and after several more minutes a light yellow color, after which a second oortion was added; now the color change took place more rapidly, whereupon a third portion was added, etc. The mixture gradually warmed up and the ether began to reflux gently. The total time required for the addition of the nitrite was about ninety minutes. Stirring and bubbling of hydrogen chloride were continued for another fifteen minutes and the mixture then was allowed to stand overnight, during which time it became quite dark. The next day the ethereal solution was slowly stirred into dilute sodium hydroxide containing pieces of ice and the ethereal layer was repeatedly extracted with cold alkali until no more product was obtained. The alkaline extracts were slowly stirred into concentrated hydrochloric acid containing sufficient ice to keep the reacting mixture cold. In this manner white crystals of isonitrosopropiophenone were obtained; these were recrystallized from toluene and melted at 106.0–106.5°;[21] yield, 71 g., or 72.5% of the theoretical. When treated with hydroxylamine (hydrochloride) in alkaline solution for several hours it formed, on acidifying, a voluminous precipitate which was recrystallized from alcohol and melted at 230.5–231.0'; this agrees with the melting point given for phenylmethylglyoxime by Gudeman and Borsche[22] who prepared it from $C_6H_5C(=NOH)COCH_3$.

***p*-Tolyl-α-oximino-ethyl** ketone was prepared after the manner described for isonitrosopropiophenone, except that 88.8 g. of *p*-tolylethyl ketone (0.6 mole) was substituted for the propiophenone; yield, 78.5 g. of the twice recrystallized isonitroso ketone, or 74% of the theoretical. The crystals, from toluene, were white flakes and melted at 125°.

Anal. Calcd. for $C_{10}H_{11}O_2N$: N, 7.91. Found: (Kjeldahl) N, 7.90.

***p*-Tolylmethylglyoxime,** prepared as was the phenyl homolog, decomposed at 230° (uncorr.), as recorded by Gudeman and Borsche.[22]

Phenylpropanolamine.—With catalyst prepared as previously described[12] from 0 5 g. of palladium chloride and 3 g of charcoal, it was possible to reduce two portions of 9.8 g. of isonitrosopropiophenone (0.06 mole), dissolved in 150 cc. of absolute alcohol containing 7.0 g. of hydrogen chloride, to phenylpropanolamine in from 145 to 190 minutes with yields of the isolated hydrochloride from 9.4 g. to 11.0 g., or 84 to 98% of the theoretical. After recrystallization from absolute alcohol the salt melted at 191°, which is the value given by Calliesz[7] and Eberhardt.[7]

The free base was obtained by treating an aqueous solution of the hydrochloride with alkali; on cooling, the liberated amino alcohol solidified and after recrystallization from water melted at 103°, which agrees with the melting point given by Hunnius and Rabe.[9]

When isonitrosopropiophenone was reduced in the absence of hydrogen chloride, the reduction proceeded very slowly and not to completion: *e.* g , 3.3 g. of isonitroso ketone in 75 cc. of absolute alcohol absorbed in six hours 1280 cc. of hydrogen (calculated for reduction to phenylpropanolamine, 1350 cc.), but from the product there was isolated only 1.3 g. of material which melted at 108–110°; when this was mixed with known phenylpropanolamine, the melting point ranged from 70 to 80°. This product was not identified.

***p*-Tolylpropanolamine** was obtained as the hydrochloride by reducing the *p*-tolyl-α-oximino-ethyl ketone under the conditions described for phenylpropanolamine. The hydrochloride, after recrystallization from absolute alcohol, melted at 205°.

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[21] The melting point given in Beilstein's "Handbuch," 4th ed., Vol. VII, p. 678, varies from 108 to 115°.

[22] Gudeman and Borsche, *Ber.*, 40, 740 (1907).

Anal. Calcd. for $C_{10}H_{15}ON \cdot HCl$: Cl, **17.59;** N, **6.95.** Found: Cl (as AgCl), **17.49, 17.62; N** (Kjeldahl), **7.04.**

The free base, isolated as was phenylpropanolamine, melted at **112°.**

Anal. Calcd. for $C_{10}H_{15}ON$: N, 8.48. Found: N (Kjeldahl), **8.53, 8.63.**

Deamination.—A solution was prepared of **6** g. of *p*-tolylpropanolamine hydrochloride **(0.03** mole) in **200** cc. of water and **15** cc. of acetic acid; it was cooled to **7°** and to it was slowly added a solution of **6.2** g. of sodium nitrite **(0.09** mole) in **35** cc. of water; the mixture was allowed to stand at room temperature for twenty-four hours, was neutralized with sodium carbonate and extracted with ether. From about one-third of the extract the ether was allowed to evaporate spontaneously and the residue was treated in the regular way to form semicarbazone; there was no evidence of its formation. The remainder of the ethereal solution was dried and distilled. The high-boiling product formed a semicarbazone melting at 191°; mixed with known semicarbazone of *p*-tolylethyl ketone there was no change in the melting point.

Phenylpropanolamine was deaminated under similar conditions. From a fourth of the ethereal extract the ether was evaporated on the steam-bath; the residue formed no semicarbazone. From a second fourth the ether was evaporated, the residue heated to boiling but not distilled and treated to form semicarbazone; after standing for ten days a very small yield of crystals was obtained, insufficient to recrystallize. The remainder of the ethereal solution was distilled; that boiling at 210–220° formed a semicarbazone that melted at **177.5°,** the semicarbazone of propiophenone.

Thus it appears that the deaminated product must be distilled before it will form a semicarbazone.

Summary

1. Phenylpropanolamine and p-tolylpropanolamine have been prepared by reducing the appropriate isonitroso ketones catalytically.
2. The method appears to be of general application and is being extended.
3. The two compounds discussed show physiological activity paralleling that of ephedrine. Further pharmacological studies are being made.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 30]

THE ALIPHATIC DIOLEFINS. II. THE PREPARATION AND SOME PHYSICAL CONSTANTS OF Δ-1,5-HEXADIENE

BY FRANK CORTESE[1]

RECEIVED APRIL 10, 1929 PUBLISHED JULY 5, 1929

In connection with some previous work on Δ-1,5-hexadiene,[2] it was noticed that great confusion existed among the physical constants recorded in the literature. Accordingly, the hydrocarbon was made from two different sources and the following accurate concordant constants were determined: . boiling point, dt/dp, melting point, density and refractive index.

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[1] Research Associate, Massachusetts Institute of Technology.

[2] Cortese, *Ber.*, 62, **504 (1929).**

Δ-1,5-Hexadiene, or diallyl, has been made by the following methods: by the action of sodium,[3] or sodium–tin alloy,[4] on allyl iodide; by the dry distillation of allyl mercuric iodide[5,6]; from allyl bromide, sodium and a few drops of alcohol (anhydrous ether was also a catalyst); from allyl iodide, zinc and a little formic ether[7] or ether;[8] from allyl iodide, aluminum and ether;[9] from 1,2,3-tribromopropane, magnesium and ether.[10] Almost all workers mention that the existing methods give poor yields and *a* poor quality of product. Undoubtedly this is due to the fact that specific directions are not given, for one worker will get a very low yield with a method which gave a good yield to another worker.

We have adopted the convenient method of causing allyl bromide to react with magnesium in the presence of ether.[11] This is an abnormal Grignard reaction, the magnesium seemingly acting as a coupling agent.[12]

Experimental Part

Preparation of Δ-1,5-Hexadiene from Allyl Bromide.—The allyl bromide was made from allyl alcohol and 48% hydrobromic acid as described in a previous paper[13] from this Laboratory.

Seventy-five grams of magnesium turnings is covered with 150 cc. of dry ether in a 2-liter flask. Six hundred grams of allyl bromide is run in as fast as possible, without stirring. It is best to add about 5 g. and wait until the reaction starts and subsides. The rate of reflux will determine the rate of addition. When the reaction stops, 50 cc. of ether is added and all is refluxed gently for five hours. The mixture of diallyl, unchanged bromide and ether is distilled from an oil-bath whose temperature is gradually raised to 250°. The distillate is dried with sodium and added to *25* g. of magnesium turnings in a one-liter flask. Fifty cc. of ether is added and a small crystal of iodine. If the reaction does not start spontaneously, a *micro burner* is used to induce it. When the reaction subsides, refluxing is continued gently for three hours. After cooling, one cc. is pipetted out and a little magnesium added to it. If there is still a reaction after standing for a few hours, fresh metal is added to the main hatch and the refluxing continued. When the indicated test is negative, all is distilled from an oil-bath, gradually raised to 140°. The distillate is shaken with ordinary concentrated hydrochloric acid[14] with cooling under the tap. The layers are separated and the process is repeated five times. Each time a volume of acid equal to that of the hydrocarbon residue is used. Finally, it is washed once with 10% sodium hydroxide and once with water. After a

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[3] Berthelot and Luca, *Ann. chim. phys.*, [3] *48*, 294 (1856).

[4] Wurtz, *ibid.*, [4] 3, 155 (1864).

[5] Linnemann, *Ann.*, 140, 180 (1866).

[6] Oppenheim, *Ber.*, 4, 670 (1871).

[7] Sorokin, *J. prakt. Chem.*, [2] 23, 1 (1881).

[8] Blaise, *Compt. rend.*, 138, 285 (1904).

[9] Domanizki, *Chem. Zentr.*, I, 982 (1915).

[10] Krestinski, *ibid.*, I, 2056 (1927).

[11] Lespieau, *Ann. chim. phys.*, [8] 27, 149 (1912).

[12] Gilman and McGlumphy, *Bull. soc. chim.*, [4] 43, 1322 (1928).

[13] McCullough and Cortese, THIS JOURNAL, 51, 225 (1929).

[14] Lucas and Dillon, *ibid.*, 50, 1461 (1928), used aqueous perchloric acid to remove ether from butene-1.

preliminary short shaking with calcium chloride, it is dried over sodium. The amount of this crude hydrocarbon is 70–75% of the theoretical based on the allyl bromide. The rest of the yield is taken up by by-products, a yellowish oil covering the magnesium bromide etherate and a copious evolution of gas when water is added to this etherate residue. These were not investigated. The yield, boiling between 59–60°, is 68%. There are no low- or high-boiling fractions. The yield boiling between 59.4 and 59.6° at 760 mm. is 36%.

From **Allyl** Chloride.—Exactly analogous procedures were used. The crude yield was 68%. The yield boiling between 59 and 60° was 55%, and the yield boiling between 59.4 and 59.6° was only 27%.

Purification.—The two samples of Δ-1,5-hexadiene were each distilled four times from fresh sodium, through a Widmer[15] column. **A** distillation curve was made each time and the appropriate cut taken from the flat portion of the curve. The final samples boiled constantly, 30 cc. from the allyl bromide run and 55 cc. from the allyl chloride run. They were halogen free as shown by sodium fusion-silver nitrate tests.

TABLE I

PHYSICAL CONSTANTS OBTAINED FOR Δ-1,5-HEXADIENE

The samples prepared from allyl bromide and allyl chloride are designated **A** and B, respectively.

Constant	A	B	Mean
B. p., °C.	$59.65 \pm 0.05°$ at 762.9 ± 0.1 mm.	$59.60 \pm 0.05°$ at 757.6 ± 0.1 mm.	$59.57 \pm 0.05°$ at 760.0 ± 0.1 mm.
dt/dp (750–770 mm.)	0.026	0.028	0.027 ± 0.001
M. p. or f. p.[a]	-140.85	$-141.1, -141.2$	-140.9 ± 0.1
d_4^0	0.7106 ± 0.0002	0.7106 ± 0.0002	0.7106 ± 0.0002
d_4^{25}	0.6863 ± 0.0002	0.6863 ± 0.0002	0.6863 ± 0.0002
n_D^{15}	1.4076 ± 0.0002	....	1.4076 ± 0.0002
n_D^{20}	1.4044 ± 0.0002	....	1.4044 ± 0.0002
n_D^{25}	1.4012 ± 0.0002	1.4012 ± 0.0002	1.4012 ± 0.0002

[a] By Dr. E. L. Skau, National Research Fellow.

The determinations of the melting point and freezing point were kindly made by Dr. E. L. Skau[16] in a special apparatus. His remarks were as follows: "Good heating curves were obtained on Sample A, although a cooling curve was not run. On Sample B cooling curves were run which were checked within 0.1° by heating curves. Both cooling and heating curves were reproducible within themselves within 0.04°. The shape of the curves obtained indicated that Sample **A** was purer than Sample B. From the amount of water and gas observed, when the samples were vacuum distilled, and from the shape of the curves, it was also concluded that the true density of diallyl had probably been determined to at least ±0.0003.

"The methods used and the interpretation of the heating curve as a criterion of purity will be discussed in a forthcoming paper."

[15] Widmer, *Helv. Chim. Acta*, 7, 59 (1924).

[16] National Research Fellow.

The writer also reached the conclusion that Sample A was the purer one from the distillation characteristics of A and B.

Pure diallyl does not have a sharp odor, as sometimes claimed. It has a very penetrating, highly "unsaturated," nauseating odor, inducing anesthesia easily. It has a sweet taste when highly diluted with water. It must be kept in a sealed bottle as it is very volatile. Ordinary samples develop a sharp odor and deposit a yellow oil on standing; purified material in sealed tubes evidently keeps indefinitely. It can be conveniently identified by the preparation of the cyclic, crystalline, neutral, monosulfuric acid ester of hexane-2,5-diol, which melts at 90° corr.[2]

Summary

1. Detailed directions are given for the preparation of Δ-1,5-hexadiene from allyl halides and magnesium in ether.

2, The boiling point, dt/dp, melting point, density and refractive index of Δ-1,5-hexadiene have been accurately determined.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, AND PROM THE RESEARCH LABORATORY, ELI LILLY AND COMPANY, INDIANAPOLIS, INDIANA]

SYNTHESIS OF EPHEDRINE AND STRUCTURALLY SIMILAR COMPOUNDS. III. A NEW SYNTHESIS OF ORTHO-DIKETONES

BY HAROLD W. COLES, RICHARD H. F. MANSKE AND TREAT B. JOHNSON

RECEIVED APRIL 12, 1929 PUBLISHED JULY 5, 1929

The synthesis of ephedrine described in Papers I and II[1,2] necessitated the preparation of considerable quantities of 1-phenylpropane-1,2-dione. This substance has been prepared by the decomposition of isonitrosoethylphenyl ketone by means of dilute sulfuric acid[3] or by means of amyl nitrite.[4] In the first case decomposition is slow and in the second case by-products are formed in large amount so that the yield of diketone in either case is small. In view of the great stability of this oxime it is not surprising that the carbonyl group with which the hydroxylamine is associated displays sufficient affinity to combine readily with primary amines—a reaction upon which the synthesis of ephedrine depends.[5] The formation of a crystalline hydrate of benzoylformaldehyde is another

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[1] Manske and Johnson, THIS JOURNAL, 51,580 (1929).

[2] Manske and Johnson, *ibid.*, 51, 1906 (1929).

[3] Pechmann and Muller, *Ber.*, 21, 2119 (1888); *ibid.*, 22, 2128 (1889).

[4] Manasse, *ibid.*, 21,2176 (1888).

[5] The authors desire to call attention to two errors which occur in the first paper; *ethylbenzyl* (line 18, p. 581) should read *ethylphenyl,* and *specially* (line 2, p. 582) should read *spatially.*

illustration of this reactivity. The dialkyl isonitroso ketones are readily convertible to diketones by means of formaldehyde, but thus far the authors are not aware of a case in which alkylaryl isonitroso ketones can be similarly decomposed. The ease of oxidation of dialkylmalonates to the corresponding mesoxalates by interaction with oxides of nitrogen is well known.[6] Gilman and Johnson[7] have recently developed further the utility of this change and have shown that nitrogen tetroxide serves as the most practical reagent for accomplishing this oxidation. The success of this work suggested the possibility of using this oxide for the oxidation of the methylene group of ethylphenyl ketone. Fortunately the reactivity conferred on the methylene carbon atom by the phenyl and carbonyl groups is sufficient not only to provide a point of attack for the nitrogen tetroxide but also to lend sufficient stability to the resulting diketone to prevent complete disintegration by the further action of the oxidant, although it has not been possible to prevent the formation of benzoic acid in considerable quantities. The yield of pure diketone, though leaving much to be desired, is still greater than that by any other feasible method, and in point of time and attention required, the authors greatly prefer this method.

Ketonic aldehydes are oxidized with great facility and their preparation by this method has not been accomplished. Obviously hydroxy ketones do not lend themselves to the reaction. The authors are inclined to believe from present evidence that isonitroso ketones are intermediate products in the reaction, although a thorough search in the case of ethylphenyl ketone yielded no oxime. It would appear that the oxime presents less stability to nitrogen tetroxide than does the ketone. In one instance, a-hydrindone, the isonitroso ketone is more resistant to the action of the oxide than the unchanged ketone, so that the former is conveniently prepared by the action of nitrogen tetroxide on the latter. In fact, isonitroso-a-hydrindone exhibits considerable stability toward nitrogen tetroxide and when reaction does ensue deep-seated changes result and no diketo-hydrindone could be isolated from the reaction product. Thus far no synthesis of this interesting diketone has been accomplished. Hot dilute acids resinify the oxime, whereas sodium bisulfite[8] forms a resinous mixture as final product. The action of aqueous formaldehyde is unusual in that the oxime is readily soluble in the commercial 35% solution; on cooling the unchanged compound crystallizes out.

A second case of abnormality in cyclic ketones is that of α-ketotetrahydronaphthalene. Here the action of a small amount of nitrogen tetroxide induces rapid and complete decomposition. The product of the

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[6] Bouveault and Wahl, *Compt.* rend., 137,196 (1903).

[7] Gilman and Johnson, THIS JOURNAL, 50,3341 (1928).

[8] Müller and Pechmann, Ber., 22,2557 (1898).

reaction consisted of comparatively insoluble resins from which neither unchanged ketone, diketone nor isonitrosoketone could be isolated.

The examples given in the experimental section suffice to show that the reaction here discussed is sufficiently general to serve as a useful method of preparing alkylaryl diketones,

Experimental Part

1-Phenyl-1,2-propanedione.—A mixture of ethylphenyl ketone (134 g.), finely powdered anhydrous calcium chloride (35 g.) and alcoholic hydrogen chloride (1 cc.), contained in a flask provided with an efficient mechanical stirrer, an inlet tube for the entry of the nitrogen tetroxide and an exit tube to accommodate the evolved gases, is treated with a stream of nitrogen tetroxide, the temperature being maintained at 60°. It is advisable to stir vigorously and introduce about 60 g. of the gas from a weighed tube in the course of three to four hours. Although there is considerable unchanged ketone in the reaction mixture at this stage, it is advisable to interrupt the reaction, since a point is reached where the rate of decomposition of diketone is nearly equal to the rate of its formation.

The reaction mixture is cooled somewhat and taken up in ether. The ethereal solution is washed with water, then exhaustively with aqueous sodium bicarbonate and finally with water. The ether is distilled from the solution and the residue distilled under reduced pressure. Distillation is continued until the residue begins to decompose. The distillate is treated with an equal volume of alcohol and vigorously shaken with 60 cc. of a saturated aqueous solution of sodium bisulfite. In the course of a few minutes, a colorless crystalline solid separates and the mixture gradually becomes pasty, the yellow color fading almost completely. The mixture is then cooled, filtered with suction and the solid washed with alcohol and finally with a little ether.

The bisulfite compound is conveniently decomposed by treatment with a warm solution of sodium carbonate. After cooling the diketone is extracted with ether, the solvent distilled and the diketone distilled in a rapid current of steam. The diketone is recovered from the steam distillate by extraction with ether and after drying and removal of solvent is distilled under reduced pressure. The yield of pure product boiling at 126–128° at 20 mm. is 26 to 28 g.

The filtrate from the bisulfite compound may be worked up for the recovery of unchanged ethylphenyl ketone by addition of water and extraction with ether. The amount recovered varies from 60 to 70 g.

Other Diketones.—Without further modification the above procedure was applied to the synthesis of a number of other diketones. Those listed below were used in the synthesis of substituted ephedrines, and the authors regard the successful isolation of the expected ephedrines as sufficient evidence of identity of the diketones: 1-phenyl-1,2-butanedione, b. p. 130–132° at 20 mm.; 1-*p*-ethylphenyl-1,2-propanedione, b. p. 138–140° at 20 mm.; 1-(2,5-dimethylphenyl)-1,2-propanedione, b. p. 140–144° at 20 mm.

The yields in all cases varied between 30 and 40%. The corresponding substituted benzoic acid was isolated in considerable quantities. It is interesting to note that the *p*-ethyl derivative is devoid of the piercing unpleasant odor characteristic of the other diketones. Its odor is strongly reminiscent of anisaldehyde, although slightly more aromatic.

Isonitroso-α-hydrindone.—A solution of 52.8 g. of α-hydrindone in 50 g. of dry benzene containing a few drops of alcoholic hydrogen chloride was cooled in ice and treated with a stream of nitrogen tetroxide until the green color persisted for about one minute after stopping the entry of the gas. An equal volume of petroleum ether was cautiously added, the cooled mixture filtered and the oxime washed first with a mixture of benzene and petroleum ether and then with the latter. The yield was 25 g. After one recrystallization it melted at 210° (corr.) alone or admixed with an authentic specimen.[9] The mother liquor yielded 25 g. of unchanged a-hydrindone when it was washed with dilute alkali, dried and distilled under reduced pressure.

This is the fifth communication submitted during the tenure by one of us of the Eli Lilly and Company Fellowship.[10] The authors desire to express their appreciation not only to the executive staff of this company for the privilege thus enjoyed, but also to the members of the technical staff for their generous cooperation.

Summary

1. A new synthesis of alkylaryl diketones which promises to be quite general is described.

2. The synthesis of a cyclic *o*-diketone was not accomplished.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

TETRA-ARYLDIARSYLS. I[1]

BY F. F. BLICKE AND F. D. SMITH[2]

RECEIVED APRIL 26, 1929 PUBLISHED JULY 5, 1929

In view of the fact that tetra-arylhydrazines[3] and hexa-arylethanes[4] dissociate spontaneously into diarylnitrogen radicals and triarylmethyls, respectively, it seemed possible that tetra-aryldiarsyls might behave in a similar manner

$$\begin{aligned} R_2As{-}AsR_2 &\rightleftharpoons 2R_2As{-} \\ R_2N{-}NR_2 &\rightleftharpoons 2R_2N{-} \\ R_3C{-}CR_3 &\rightleftharpoons 2R_3C{-} \end{aligned}$$

Several investigators have studied tetraphenyldiarsyl with regard to its tendency to dissociate into diphenylarsyl. Schlenk[5] determined the molecular weight of the substance in boiling benzene but found no evidence of dissociation. According to Porter and Borgstrom,[6] as well as Borgstrom and Dewar,[7] molecular weight determinations in naphthalene by the cryo-

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[9] Gabriel and Stelzner, Ber., 29, 2604 (1896).

[10] Richard H. F. Manske.

[1] This paper represents the third part of a dissertation submitted to the Graduate School by Mr. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Parke, Davis and Company Fellow, 1927–1929.

[3] Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, 1913.

[4] References to the literature on hexa-arylethanes is to be found in "Organic Radicals," Gomberg, Chemical *Reviews*, 1, 141 (1924); also in Walden, "Chemie der frieien Radikale," S. Hirzel, Leipzig, 1924.

[5] Schlenk, *Ann.*, 394, 220 (1912).

[6] Porter and Borgstrom, THIS JOURNAL, 41, 2051 (1919).

[7] Borgstrom and Dewar, *ibid.*, 44, 2919 (1922).

scopic method indicate that tetraphenyldiarsyl is associated rather than dissociated.

It seemed to us that more favorable results might be obtained in the case of tetra-p-anisyl-, tetra-α-naphthyl- and tetrabiphenyldiarsyl; at least it has been found that the anisyl, naphthyl and biphenyl nuclei further dissociation in the hexa-arylethane group.[8]

We decided to investigate these tetra-aryldiarsyls and had intended to prepare them by reduction[9] of the tetra-arylarsyl oxides, since satisfactory methods of preparation for these oxides have been developed.[10] However, a much simpler procedure was found. The tetra-arylarsyl oxides are converted readily by the action of hydrogen chloride into the diarylarsyl chlorides and the latter react with sodium iodide to form the corresponding iodides. Interaction of the latter with metals, at ordinary temperature, yields the tetra-aryldiarsyls. For example, the halogen is removed quantitatively if diphenylarsyl iodide, dissolved in bromobenzene,[11] is shaken vigorously with mercury for twenty minutes. Such a solution, in less than thirty seconds, absorbs almost exactly the quantity of oxygen[12] calculated for the formation of a peroxide, $(C_6H_5)_2As\text{-}O\text{-}O\text{-}As(C_6H_5)_2$ and decolorizes instantly a carbon tetrachloride solution of iodine.

In fact, the solution obtained after removal of the halogen from diphenylarsyl iodide is strikingly similar in behavior toward oxygen and iodine to that obtained when triphenylmethyl chloride, dissolved in bromobenzene, is treated with mercury; however, in the former case the solution is colorless, in the latter it is yellow.

In order to obtain tetraphenyldiarsyl in the solid state, diphenylarsyl iodide was dissolved either in benzene or absolute ether and, after removal of the halogen by mercury, the solution was filtered and the solvent removed under diminished pressure. During these operations precaution must be taken to prevent oxygen from coming in contact with the material. The crystalline diarsyl, when dissolved in bromobenzene, absorbs the amount of oxygen calculated for peroxide formation.

The behavior of tetraphenyldiarsyl and other tetra-aryldiarsyls described in this paper indicates that these compounds dissociate to some

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[8] In the tetra-arylhydrazine series, according to Wieland, tetra-*p*-anisylhydrazine dissociates to a greater extent than tetraphenylhydrazine but tetrabiphenylhydrazine undergoes less dissociation than the phenyl analog.

[9] Michaelis and Schulte, Ber., **15,** 1952 (1882).

[10] Blicke and Smith, THIS JOURNAL, **51,** 1558 (1929).

[11] This solvent was chosen because of its comparatively low vapor pressure, an essential feature if the solution is to be used subsequently for an oxygen-absorption determination. As far as the removal of halogen and formation of the diarsyl is concerned, other solvents such as ether or benzene serve equally well.

[12] The apparatus devised by Gomberg and Schoepfle, THIS JOURNAL, 39, 1661 (1917), for oxygen absorption was employed.

extent into diarylarsyls, that is, divalent arsenic radicals. Molecular weight determinations of the various diarsyls are now being carried out in the hope that the dissociation, in some cases at least, is of such a magnitude that it can be detected by this method.

The behavior of other diarylarsyl iodides with mercury is described in the experimental part of this paper.

A further study of tetra-aryldiarsyls is in progress in this Laboratory and the action of metals on diarylstibinyl halides and on diarylbismuthyl halides is being investigated.

Experimental Part

Diphenylarsyl iodide, dissolved in bromobenzene, ether or benzene, reacts very rapidly at ordinary temperature with mercury, slower with molecular silver and zinc powder and very slowly, if at all, with magnesium powder or magnesium ribbon. In one instance $^1/_{200}$ mole of diphenylarsyl iodide, 6 g. of mercury and **15** *cc.* of bromobenzene were placed in the absorption bottle and the mixture was shaken continuously by hand. The amount of oxygen which had reacted after twenty minutes was **56** cc.; after thirty minutes, 59 cc. No further amount of oxygen was absorbed after an hour. The calculated quantity of oxygen required for peroxide formation is **56** *cc.*

A mixture prepared from 6 g. of mercury, 0.6 g. of iodine and **15** cc. of bromobenzene was rotated for four hours in a sealed tube. The mixture did not absorb oxygen; neither did diphenylarsyl iodide dissolved in bromobenzene absorb the gas.

It was found by analysis[13] of the mercury halide formed that mercury removes the halogen rapidly from di-*p*-tolyl-, di-*p*-anisyl-, di-α-naphthyl- and dibiphenylarsyl iodide.

Bromobenzene solutions obtained by shaking diphenyl-, di-p-tolyl- and di-p-anisyl iodide, respectively, with mercury, after complete removal of the iodine, absorb at once the calculated quantity of oxygen with the evolution of a considerable amount of heat. If the solution which has absorbed oxygen is allowed to remain in contact with the gas for a long period of time, a further *slow* absorption takes place due, probably, to the decomposition of the peroxide into secondary products which react with oxygen. **A** similar behavior is characteristic of triarylmethyl peroxides. In the case of solutions obtained from di-a-naphthyl- and dibiphenylarsyl iodide there was an immediate absorption of oxygen in excess of that required for the formation of a peroxide, the absorption varying from 125–130% of the calculated amount. At present we are unable to account for this phenomenon.

Relation between the Quantity **of** Oxygen Absorbed and the **Amount of** Halogen Removed.—Two sets of sealed tubes were rotated for definite periods of time. Each tube of the one set contained $^1/_{200}$ mole of diphenylarsyl iodide, **15** cc. of bromobenzene and **3.0** g. of molecular silver **(80–100** mesh). Each tube of the second set contained one-fifth of the above quantities of material. At intervals one tube from each set was removed from the rotating apparatus. The tube which contained the larger quantities was used for oxygen absorption; the contents of the other tube were poured on a filter, the residue of silver and silver iodide was washed several times with boiling xylene and then with acetone. The mixture was removed from the filter and the silver dissolved with hot, dilute nitric acid. The silver iodide was filtered and weighed.

A comparison of Line 4 with Line 3 shows that the percentage of oxygen absorbed is comparable, within the limit of experimental error, to the

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[13] The analytical procedure of Kohn, *Z. anorg. Chem.*, 59, 108 (1908), was used but the iodine was determined volumetrically by the Volhard method.

percentage of silver iodide formed. The actual amount of oxygen absorbed, Line 2, is practically the same as that calculated, Line 5, from the quantity of silver iodide.

TABLE I

EXPERIMENTAL DATA

Time shaken, hours	6	11	24	48
O_2 abs. after 1 min., cc,, N.T.P.	14	26	41	53
Silver iodide. %	22	44	72	94
Oxygen absorbed, %	25	46	73	95
Abs. calcd. from AgI, cc.	12	25	40	52

It was found that diphenylarsyl iodide and triphenylmethyl bromide react instantly, when dissolved in bromobenzene, to form a deep red solution. The tendency for reaction is so great that when the two compounds are mixed in the solid state a red color develops at the points of contact. The solution absorbs oxygen rapidly. Undoubtedly the two compounds react in accordance with the following equation

$$(C_6H_5)_2AsI + (C_6H_5)_3CBr = (C_6H_5)_2AsBr + (C_6H_5)_3CI;\ (C_6H_5)_3CI \rightleftharpoons (C_6H_5)_3C- + I$$

However, the volume of oxygen absorbed (50 cc.) is greatly in excess of that calculated (28 cc.) for the amount of triphenylmethyl which could be produced. Other diarylarsyl iodides behave in an entirely analogous manner with triphenylmethyl bromide,

No color was developed when a mixture of diphenylarsyl bromide and triphenylmethyl bromide was dissolved in bromobenzene, and the solution did not absorb oxygen. No oxygen was absorbed by a mixture of diphenylarsyl bromide, iodine and bromobenzene.

A mixture of $^1/_{200}$ mole of diphenylarsyl iodide, 3 g. of silver and 15 cc. of bromobenzene was rotated for two days. The mixture absorbed 56 cc. of oxygen or 100% of the calculated amount. A similar mixture, except that $^1/_{200}$ mole of triphenylmethyl bromide was used in place of the arsyl iodide, absorbed under similar conditions 52 cc. of oxygen or 93% of the calculated amount. One four-hundredth mole of diphenylarsyl iodide, $^1/_{400}$ mole of triphenylmethyl bromide, 3 g. of silver and 15 cc. of bromobenzene were rotated for two days; the mixture absorbed 73 cc. of oxygen or 130% of the calculated amount.

Preparation and Properties of Tetraphenyldiarsyl.[14]—One-hundredth mole of diphenylarsyl iodide, 12 g. of mercury and 60 cc. of dry benzene[15] were put into a bottle which had been filled previously with dry, oxygen-free nitrogen. The bottle was stoppered tightly and then shaken by fastening it to the rim of a slowly revolving wheel. After the halogen had been removed the mixture was filtered into an apparatus similar to that used for the isolation of triarylmethyls.[16] The bulb of the apparatus was placed in a cone-shaped coil made from lead pipe, steam was passed through the latter

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[14] This procedure applies also to the preparation of tetra-*p*-tolyldiarsyl and tetra-p-anisyldiarsyl.

[15] The benzene had been saturated with dry, oxygen-free nitrogen and was preserved over sodium. Ether may be used in place of benzene as a solvent:

[16] Gomberg and Cone, *Ber.*, 37, 2033 (1904).

and most of the solvent in the bulb was removed under diminished pressure.[17] The greater portion of the diarsyl separates as a colorless, crystalline precipitate. The contents of the bulb were treated with 20 cc. of dry, oxygen-free ether and the liquid poured out of the apparatus. The precipitate was dried by applying suction to the bulb and maintaining the latter at a temperature of 70–80° for three hours to insure complete removal of the solvent. The apparatus was then filled with nitrogen and the diarsyl transferred to a small test-tube in a stream of the gas.[18] The compound melted at 120–125°.[19]

In several instances oxygen absorptions were made with the tetraphenyldiarsyl isolated from ether. It was found that 0.5440 g. of the diarsyl, dissolved in bromobenzene, absorbed after one minute 26 cc. (calculated amount, 26.5 cc.). In a second experiment 0.5005 g. of the material was dissolved in ethylene bromide. The solution absorbed 25 cc. (calculated amount, 24 cc.).

Potassium permanganate dissolved in acetone was added to tetraphenyldiarsyl dissolved in the same solvent. The diarsyl decolorized instantly the amount of permanganate required theoretically to convert the substance into diphenylarsinic acid, although the latter was not isolated. Tetraphenylarsyl oxide and diphenylarsyl iodide also decolorized immediately an acetone solution of potassium permanganate.

Tetraphenyldiarsyl, tetraphenylarsyl oxide and diphenylarsyl iodide all decolorized instantly iodine dissolved in carbon tetrachloride. In the case of the tetraphenyldiarsyl the exact amount of iodine was added which was necessary for the formation of the diphenylarsyl iodide. A black, gummy precipitate formed which was, no doubt, a periodide. The solution was decanted from the precipitate and after removal of the solvent the black, viscous residue was covered with water and treated with sulfur dioxide. A yellow, crystalline substance was obtained which, after recrystallization from alcohol, melted at 42–43°. This material was diphenylarsyl iodide.

That a solution of tetraphenyldiarsyl is stable toward light, at least in the presence of mercury salts, is shown by the following experiment: 1.78 g. ($^1/_{200}$ mole) of diphenylarsyl iodide, 6 g. of mercury and 15 cc. of bromobenzene were rotated for eighteen hours. The tube which contained the material was then placed outdoors for nineteen days. The contents of the tube absorbed the calculated amount of oxygen, that is, 56 cc.

Summary

It has been shown that a number of tetra-aryldiarsyls can be prepared readily, from the interaction of a diarylarsyl iodide and mercury.

Because of the extremely great reactivity of these compounds toward oxygen, and other reagents, it seems that their behavior can be explained best by the assumption that the tetra-aryldiarsyls dissociate spontaneously into diarylarsyls, that is, divalent arsenic radicals.

ANN ARBOR, MICHIGAN

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[17] If all of the solvent was removed, the diarsyl obtained was somewhat gummy.

[18] The diarsyls are so extremely reactive toward oxygen that it was found advisable to remove the compound from the apparatus in a large, specially designed box which was filled with dry carbon dioxide. All operations which involved exposure of the diarylarsyl, such as the preparation of pellets for molecular weight determinations, were carried out in this box.

[19] Michaelis and Schulte, ref. 9, state that the compound melts at 135°; Borgstrom and Dewar, ref. 7, recorded the melting point as 130.5° (corr.).

NOTES

A Note on the Use of Aniline in the Preparation of Amino Acids.—A standard method of isolating certain amino acids is to precipitate them from the alcoholic solutions of their hydrochlorides with pyridine. Cox, *J. Biol. Chem.*, 78, 475 (1928), used aniline in preparing d-arginine monohydrochloride. A consideration of the basic ionization constants of glycine, alanine and aniline indicated that aniline should precipitate these amino acids from their hydrochlorides, Experiment justified this prediction. Glycine can be prepared by the method of Clarke and Taylor, "Organic Syntheses," 4, 31 (1925), using aniline instead of pyridine. Alanine has been prepared by mixing acetaldehyde (1 mole), aqueous ammonium chloride (2 moles), and sodium cyanide (1 mole), and hydrolyzing by concentrated hydrochloric acid. This solution is then evaporated under reduced pressure to a thick paste, treated with absolute methanol (10 moles), filtered to remove solid chlorides and treated with aniline (1.3 moles). The yield of recrystallized alanine is 50% of the theoretical amount.

α-Amino-*iso*butyric and a-amino-n-valeric acids can be easily prepared in a similar manner.

CONTRIBUTION FROM THE
DENTAL SCHOOL
NORTHWESTERN UNIVERSITY
CHICAGO, ILLINOIS

H. C. BENEDICT

RECEIVED JANUARY 28, 1929
PUBLISHED JULY 5, 1929

β,β-Dinaphthyl Sulfide as a By-product in the Preparation of β-Naphthoic Nitrile. Reduction of the Sulfone with Sodium Cyanide.—Colver and Noyes,[1] while working on the synthesis of anthracene from naphthalene, found that the hydrolysis of the crude nitrile of β-naphthoic acid by boiling with a 30% solution of sodium hydroxide "left an unsaponifiable residue which is a reddish colored liquid at the temperature of the hot water-bath, but solidifies to a dirty red solid upon cooling. It is heavier than water, easily soluble in benzene but much more difficultly soluble in alcohol and ether." Other properties of the substance were not ascertained and no further investigation was made by them as to its identity.

Several years ago, during the course of an investigation on the preparation of certain ketones derived from β-naphthoic acid, a considerable amount of this unsaponifiable residue was accumulated and an investigation was undertaken to identify the material. It was distilled with steam, first in a concentrated alkaline solution and then in a concentrated acid solution; the non-volatile residue was separated from the water, dried and then distilled under reduced pressure. The distillate was a

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[1] Colver and Noyes, THIS JOURNAL, 43, 901 (1921).

greenish-yellow liquid which on cooling became a light yellow solid. On standing exposed to the air the surface of the material turned red; crystallization from benzene removed the impurity responsible for the red color; a second recrystallization from benzene and washing with petroleum ether gave colorless, glistening, crystalline flakes, m. p. 151°; further recrystallizations from benzene and from ethyl alcohol did not change the melting point.

Anal. Calcd. for $C_{20}H_{14}S$: C, 83.86; H, 4.93; S, 11.2. Found: C, 84.06; H, 4.88; S, 11.7.

The melting point and the analysis indicated that the compound at hand was β,β-dinaphthyl sulfide.[2] Further evidence as to its identity was obtained by the melting point remaining unchanged on mixing with a sample of pure dinaphthyl sulfide prepared by heating the lead salt of β-thionaphthol; when oxidized in acetic acid solution with potassium dichromate and sulfuric acid, β,β-dinaphthyl sulfone, m. p. 177°, was obtained.[3]

These results show that the unsaponifiable portion of crude β-naphthoic nitrile, prepared by the fusion of sodium β-naphthalene sulfonate and sodium cyanide, consists mostly of β,β-dinaphthyl sulfide; this sulfide is probably formed by the reduction of β,β-dinaphthyl sulfone

$$(C_{10}H_7)_2SO_2 + 2NaCN \longrightarrow (C_{10}H_7)_2S + 2NaCNO$$

This sulfone is formed in small quantities when naphthalene is sulfonated at 180°,[4] and is present as an impurity in the sodium naphthalene sulfonate which was used as the starting product for the synthesis of the nitrile.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
CASE SCHOOL OF APPLIED SCIENCE
CLEVELAND, OHIO

N. A. LANGE,
H. S. HAUPT

RECEIVED APRIL 5, 1929
PUBLISHED JULY 5, 1929

A New Series of Sulfonephthaleins.—In a recent article under the above title Harden and Drake, THIS JOURNAL, **51,** 562–566 (1929), a number of new compounds suitable for use as indicators for determining hydrogen-ion concentration were announced. Dr. I. M. Kolthoff, of the University of Minnesota, has kindly directed our attention to the fact that one of these compounds, tetrabromophenoltetrabromosulfonephthalein, has distinct advantages over brom phenol blue as an indicator. The new indicator shows a color change from yellow to blue, just as do brom cresol green and brom thymol blue, but without the interfering dichromatism.

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[2] Krafft and Schonherr, *Ber.*, 22, 825 (1899).

[3] Krafft, *ibid.*, 23, 2366 (1890).

[4] Stenhouse and Groves, *ibid.*, 9, 682 (1876).

Dr. Kolthoff suggests the use of the new indicator instead of brom phenol blue, and proposes the trade name of "tetrabrom phenol blue."

CONTRIBUTION FROM THE LABORATORIES OF
HYNSON, WESTCOTT AND DUNNING AND THE
UNIVERSITY OF MARYLAND
BALTIMORE AND COLLEGE PARK, MARYLAND

WILTON C. HARDEN
NATHAN L. DRAKE

RECEIVED APRIL 10, 1929
PUBLISHED JULY 5, 1929

NEW BOOKS

Polar Molecules. BY P. DEBYE, Ph.D., Professor of Physics and Director of the Physical Institute, Leipzig, Germany. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1929. 172 pp. 33 figs. 15 X 23.5 cm. Price, $3.50.

During the past four years most papers dealing with dielectric constants have contained a reference somewhere in their first two or three pages to the chapter written by Professor Debye for one of the great German physical handbooks. Now one may expect to see this replaced by a reference to the present book, which makes available in English and in convenient form the most authoritative work on the theory of dielectrics. By this the reviewer does not mean to imply that the book is a mere translation or even a revision of the massive chapter which contains the foundation of so much recent dielectric investigation. It is, rather, a new work. The theory of dielectrics founded on the classical mechanics is presented and treated in the light of the recent extensive experimental investigations. The methods of calculating electric moments are considered and the relation of the moment of the molecule to its structure is shown by material taken from the recent literature. A chapter devoted to the constitution of simple polar molecules attacks the problem by means of the potential energy of the structure as calculated by Heisenberg and Hund. The chapter on anomalous dispersion for radio frequencies has the advantage over the earlier treatment that there is now available somewhat more experimental material to which the theory may be applied. Under electrical saturation effects, a problem of great interest to the physical chemist, that of the dielectric constant of ionic solutions, is treated with a reserve that is necessitated by the discordancy of the experimental results. The last four of the ten chapters are given over to recent developments in fundamental theory, as may be gathered from a list of the principal sub-headings: the thermodynamic potential and the quantum states, the dielectric constant and the Stark effect, geometrical optics and classical mechanics, wave optics and wave mechanics, the energy levels of a rotating diatomic molecule, the dielectric constant of polar gases, probabilities of transition, the wave function of polar molecules disturbed by a periodic field, infra-red dispersion of a polar gas.

The book is written from the point of view of the physicist but touches upon many questions of interest to the chemist, who, although he may find much of it rather hard reading because of the difficulty inherent in the subject, cannot fail to be impressed by the admirable clarity of thought so characteristic of the author and by the value of this penetrating survey of dielectric behavior by the man who has done so much to develop the field.

CHARLES P. SMYTH

Technische Gase, **ihre** Herstellung und ihre **Verwendung.** (Industrial Gases, their Preparation and Uses). DR. FRANZ MUHLERT, Gottingen, and DR. KURT DREWS, Berlin. S. Hirzel, Leipzig, Germany, 1928. viii + 416 pp. 196 figs. 15 × 22.5 cm. Price, unbound, M. 22; bound, M. 24.

The book aims to give a broad survey of the field of industrial gases, showing the relation of the various gas industries to one another and to chemical and metallurgical industries. The authors have been extremely successful in presenting in concise form the fundamental chemical aspects, the engineering developments and the operating features pertaining to the manufacture of a host of industrial gaseous compounds and mixtures of these gases. The technology of the various combustible gases derived from wood, peat, "brown" coal, bituminous coal, anthracite coal, coke and oil is described in considerable detail for many processes. The book is profusely illustrated with flow diagrams of processes and photographs of equipment. Tables correlating the chemical compositions and other characteristics of the various fuels and gases are included. The treatment of the gas prior to its use, to include its purification, transportation and distribution, is described in considerable detail, reflecting the importance of this enterprise in Germany, where coke oven gas is being transported to distant cities. There is also included a compilation of statistics on the present magnitude of the combustible gas industry in Germany and the costs of gas by the various processes.

D. C. BARDWELL

Messungen elektromotorischer **Kräfte** galvanischer Ketten mit **wässerigen Elektrolyten.** (Measurements of the Electromotive Forces of Galvanic Cells with Aqueous Electrolytes.) Edited by CARL DRUCKER. Second supplementary volume. No. 10 of the Abhandlungen der Deutschen Bunsen-Gesellschaft. Verlag Chemie, G. m. b. H., Berlin W 10, Germany, 1929. viii + 234 pp. 17 × 24.5 cm. Price, M. 24.

The first supplementary volume of this compilation of electromotive-force measurements appeared in 1915. The present volume covers the literature from 1914 to the end of 1927.

The method of presentation of the earlier volumes is followed here. The book is divided into three parts. In Part I, under each element is given a chronological bibliography of the literature dealing with the electromotive force of galvanic cells containing this element. In Part II, under each element is given in chronological order a list of the electromotive-force data obtained with each cell measured. In Part III, the normal potentials calculated from these measurements are given, taking the potential of the hydrogen electrode as zero. These are listed first under the head of the various elements and second according to increasing (positive) potentials. Then follows an index according to authors of the articles cited. Finally a convenient summary of the most important normal potentials is provided on a separate card.

This careful and concise collection of electromotive-force data is a valuable one indeed, particularly in conjunction with the earlier volumes of the series.

It is of interest that the contributions from THIS JOURNAL listed in this volume far exceed in number those from any other journal.

ARTHUR B. LAMB

A Textbook of Organic Chemistry. BY JOSEPH SCUDDER CHAMBERLAIN, Ph.D., Professor of Organic Chemistry, Massachusetts Agricultural College. Second edition, revised. P. Blakiston's Son and Co., 1012 Walnut Street, Philadelphia, 1928. xxx + 901 pp. 15 × 22 cm. Price, $4.00.

In this second edition of his organic chemistry textbook, Professor Chamberlain has made some additions to the descriptive matter of the earlier publication, and has introduced two new and rather useful features, first, the placing of appropriate study questions at the end of each chapter and, second, an emphasis on the importance of literature study by introducing throughout the book numerous references to standard methods of preparation for the more common types of organic compounds. A number appearing beside a compound in the text refers the reader to the appendix, in which is given usually more than one reference to well-known laboratory guides and handbooks.

It is suitable for a first course in organic chemistry, although it covers rather more ground than is usually considered appropriate for a beginner. On the other hand, the number (901) of pages is somewhat misleading in that considerable space is devoted to thorough discussion of many of the simpler reactions. In fact this is one of the few criticisms that might be directed at the text. The subject matter is clearly and simply stated; numerous formulations—possibly too numerous in places—make for ease of reading and understanding on the part of the student.

The book as a whole appears to the reviewer to possess real merit; it should find a deserved place among the better American organic chemistry texts.

A. J. HILL

Enzyme Actions and Properties. By ERNST WALDSCHMIDT-LEITZ, Institute of Biochemistry, Prague. Translated and extended by Robert P. Walton. John **Wiley** and Sons, Inc., New York, 1929. xviii + *255* **pp.** 12 figs. **15.5 × 23.5 cm.** Price, $4.00.

So voluminous is the literature of enzyme research published during the past decade by the Willstatter school that it is a convenience to have its main results concisely collected. This Waldschmidt-Leitz has done, giving his summary the form of a general treatise on enzymes. The book is divided (using the terminology which it employs) into a General Section including development of the ferment concept, enzymes as colloids, and as electrolytes, enzymic kinetics, enzymic reaction systems, specificity, and procedures in preparative work; and a Special Section dealing with esterases, proteases and peptidases, aminoacylases, carbohydrases, catalases, peroxidases, oxidases, and fermentation enzymes. Since all this is covered in 241 pages of text, it is plain that detailed treatments of these numerous and comprehensive topics are not to be expected. Doubtless also any detailed attempt at comparative evaluation of the several chapters would be subject to large personal equation according to the individual viewpoint of the critic. In the judgment of the present reviewer, the treatment is reasonably well balanced as between topics, but on most topics is not well balanced in the selection of material. The author's predilection for the work and views of his own school has been permitted seriously to bias what is offered as a general view of the subject, and, while according to the title page the translator has extended the original text, this seems to have been done rather unevenly, so that many if not most of the chapters show an extremely partial presentation of the topics which they profess to cover. Thus, the admirable work of T. B. Osborne upon malt amylase is not even mentioned, nor do we find any reference to the very extensive work of Falk upon the lipases and esterases, nor to any of the recent American work upon the purification and chemical nature of pepsin. It seems especially unfortunate that the long preface, while plausibly written, is as badly biased as the body of the text, and its claims (as often happens) have already been reflected in more than one review. Those who read the book expecting the oriented view which the preface promised will (depending upon their background of acquaintance with enzymes) either be misled or disillusioned. The experienced and critical reader may conveniently make use of this handy little volume as a summary of the views and findings of the recent Munich school. The importance of certain of their findings will be gladly and gratefully acknowledged by all investigators of enzyme problems.

H. C. SHERMAN

The Journal of the
American Chemical Society

VOL. 51 AUGUST, 1929 No. 8

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORIES, SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

THE CRYSTAL STRUCTURE OF TRICALCIUM ALUMINATE

BY F. A. STEELE[1] AND WHEELER P. DAVEY

RECEIVED JULY 5, 1928 PUBLISHED AUGUST 7, 1929

It was predicted a number of years ago on theoretical grounds that many of the complex minerals, such as those of the polysilicic acids, would be found to contain molecules of the component oxides rather than complex ionic groups.[1a] $K_2O{\cdot}Al_2O_3(SiO_2)_6$ was cited as an example. So far, no data have been published which support this view, and, so far as the present authors know, no compounds of this type have been examined by x-ray methods. It was with the hope of obtaining data on this type of compound that this research was undertaken. Tricalcium aluminate ($3CaO{\cdot}Al_2O_3$) was chosen for analysis because it was known to be optically isotropic, thus showing that the crystals have cubic symmetry, and because of its relatively simple composition and its lack of ability to exist in other than the solid state. It is said to melt incongruently at 1535°, giving a melt of the two oxides with an excess of CaO. No method is known by which crystals of tricalcium aluminate can be grown of such size as to permit of goniometric measurements. This has necessitated the use of a very general method of application of the theory of space-groups to the powder method of x-ray crystal analysis. It turns out that tricalcium aluminate does not show the new type of structure originally sought. Instead, it is "mixed ionic," *i. e.*, the metallic elements and the oxygen all enter the compound as separate crystallographic entities. It is with the determination of this type of structure and with the sort of chemical combination which it discloses that this paper has to do.

Preparation of $3CaO{\cdot}Al_2O_3$.—A mixture of CaO and Al_2O_3 of high purity in the molecular ratio of three to one was very thoroughly mixed and ground in an agate mortar. It was then heated for about twenty minutes in a small platinum boat which was directly heated in the air by an electric current to 1350–1450°. Temperatures were measured by an optical pyrometer and were found to be substantially uniform over the

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[1] The material here presented was used by the junior author in partial fulfilment of the requirements for the Ph.D. degree at The Pennsylvania State College, June, 1928.

[1a] Langmuir, THIS JOURNAL, 38, 2241 (1916).

portion of the boat used. The substance does not fuse at these temperatures but sinters into a light, friable lump. The cycle of grinding and heating was repeated from two to eight times for each sample. Little improvement in the material could be noted after the third cycle. The temperature was not critical within the above limits.

X-Ray Diffraction Data.—X-ray diffraction patterns of the powdered substance, made on the General Electric apparatus, using molybdenum K-alpha radiation, showed strong lines characteristic of a body-centered cube, $a = 3.812$ Å., superimposed upon a weak pattern of CaO and numerous additional faint lines. Since $3CaO{\cdot}Al_2O_3$ is known from optical data to have cubic symmetry,[2] it seemed likely that the body-centered cubic lines mentioned above were due to this substance. It remained to account for the extra lines.

The optical properties of the four compounds of CaO and Al_2O_3 which have been described in the literature[2] ($3CaO{\cdot}Al_2O_3$, $5CaO{\cdot}3Al_2O_3$, $CaO{\cdot}Al_2O_3$ and $3CaO{\cdot}5Al_2O_3$) are given in the "International Critical Tables." Using these data as a basis of identification, the petrographic microscope revealed the presence of large amounts of $3CaO{\cdot}Al_2O_3$, together with smaller amounts of $3CaO{\cdot}5Al_2O_3$ and CaO. $5CaO{\cdot}3Al_2O_3$ and $CaO{\cdot}Al_2O_3$ were absent. Another batch of the material was prepared with about equal molar proportions of the two oxides. The petrographic microscope showed that it contained a much greater proportion of $3CaO{\cdot}5Al_2O_3$. The x-ray diffraction pattern showed a much greater relative intensity of all but three of the lines which had not been accounted for in the previous diffraction patterns. These three lines correspond to interplanar spacings of 3.1 Å., 2.20 Å. and 1.79 Å. These spacings may be derived from a cube whose side is twice that corresponding to the body-centered cubic pattern. These data were taken as conclusive evidence that the body-centered cubic lines, and the three additional faint lines, were due to $3CaO{\cdot}Al_2O_3$ and that the other faint lines were due to CaO and $3CaO{\cdot}5Al_2O_3$.

The interpretation of the crystal structure of tricalcium aluminate, therefore, resolves itself into a search for those structures which can quantitatively account for the body-centered cubic pattern and for the three faint lines mentioned above. The first step is the determination of the number of "molecules" per unit crystal cell.

The Number of Molecules per Unit Cell.—Since tricalcium aluminate is available only in a finely divided and relatively impure condition, a precision measurement of its density is not possible. An approximation sufficiently close for the determination of the number of molecules per unit cell was made, however, by observing the behavior of the substance in liquids of various densities. The observations were made by filling a

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[2] Shepherd, Rankin and Wright, *Am. J. Sci.*, **28, 293** (1909); Rankin and Wright, *ibid.*, **39, 1, (1915).**

fine capillary tube with a suspension of the powder in a mixture of methylene iodide and mesitylene of previously determined density. A petrographic microscope was mounted with its optical axis horizontal, and the tube containing the suspension was mounted vertically on the microscope stage. With a liquid whose density was 2.89 most of the tricalcium aluminate particles moved downward, and those of $3CaO{\cdot}5Al_2O_3$ moved upward. A partial separation of the two was obtained by centrifuging the suspension. Complete separation could not be obtained because of the mechanical union between particles due to the sintering process. The relatively pure $3CaO{\cdot}Al_2O_3$ thus obtained was dried and used in subsequent determinations. This powder was found to fall in a liquid of density 2.94 and to rise in one of density 3.07. In a liquid of density 3.005 the particles went up and down in about equal numbers. The density of $3CaO{\cdot}Al_2O_3$ is therefore between 2.94 and 3.07 and is probably very close to 3.00. The number of molecules per unit cube ($a = 3.812$ Å.) is given by the density and molecular weight as 0.373 ± 0.004. This is very nearly equal to $^3/_8$. No other common fraction whose numerator and denominator are small integers comes within the precision of the data. Since the number of "molecules" in a unit cell must be a whole number, it is evident that the edge of the unit cell must be a multiple of 3.812 Å. A cube of twice these dimensions (*i. e.*, $a = 7.624$ Å.) would contain three "molecules." A smaller cell cannot possibly contain a whole number of "molecules" without conflicting with the x-ray data. Furthermore, there are no data from the diffraction patterns which require that it be larger. This means that for crystallographic purposes the formula of tricalcium aluminate should be $9CaO{\cdot}3Al_2O_3$. The three faint lines mentioned above might be accounted for quantitatively within the precision of the data by assuming that they are caused by first-order diffraction from 2 1 1, second-order diffraction from 1 1 1 and third-order diffraction from 1 1 0, respectively. It will appear later that all three can be accounted for in this way.

The Crystal Structure.—Since the body-centered cubic pattern from the tricalcium aluminate is on the basis of a cube of one-half the dimensions of the unit cell, it must be considered to be essentially an accidental result of the atomic arrangement within the unit cell and, as such, it imposes no symmetry limitations upon the cell as a whole. Since no crystals large enough for symmetry observations or Laue photographs could be made, none of the usual methods for establishing the space-group is available. This means that every possible arrangement of the atoms consistent with cubic symmetry must be considered as a possibility until it is shown to be in conflict with known facts or data.

The procedure used in writing down the possible arrangements was essentially the same as that used by Wyckoff in his treatment of calcite[3]

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[3] Wyckoff, *Am. J. Sci.*, **50**, **317** (1920).

except that the process is greatly complicated by the fact that all cubic space-groups must be considered and that there are many more atoms to place in the unit cell. In considering the possible combinations of groups of equivalent points occupied by a given kind of atom, it is obviously necessary to consider only those numbers which represent groups. of equivalent points in cubic symmetry, namely, 1, 2, 3, 4, 6, 8, 12 and 16. Furthermore, those which do not have variable parameters, namely, 1, 2 and 3, need not be considered more than once. Bearing these limitations in mind, the possible combinations for the six Al ions are found to be 6 all alike, 4 of one kind and one each of two others, 4 of one kind and 2 of another, 3 of one kind and 3 of another, and **3** of one kind, 2 of another and one of another. These combinations may be expressed more conveniently by merely writing the possible numbers totaling 6, bearing in mind the limitations mentioned above. The possible combinations for Al are, then, 6, 4–1–1, 4–2, 3–3 and 3–2–1. This code will be followed in the subsequent discussion. Reference to the summary table[4] of equivalent points in the various space-groups of the cubic system shows that all of these are possible except the last. The 3–2–1 combination is impossible because there is no one space-group which contains arrangements of both *2* and 3 equivalent points'.

A similar treatment of the nine positions required for the Ca ions leads to the combinations 8–1, 6–3, 4–3–1–1 and 4–4–1. Each combination for Al must now be considered with each combination for Ca, and the space-groups compatible with both are written down. As may be seen in Table I, the entire list includes only five space-groups. This whole process is then repeated for the possible combinations for the 18 oxygen ions. The results are listed in Table II. Although there are only five space-groups involved, there are so many combinations possible within each space-group that the total number of possible arrangements is very large. For instance, if Ca is taken at 8c and 1a,[5] and Al at 6a, there are over **30** configurations of O possible. Since Al may also be at 6b, 6c or 6d, this number is increased four-fold. Placing Ca at 8c and 1b again

TABLE I

SPACE-GROUPS POSSIBLE FOR VARIOUS ARRANGEMENTS OF CA AND AL

Combinations for calcium	Aluminum at 6–0	Aluminum at 4–1–1	Aluminum at 4–2	Aluminum at 3–3
8–1	$T_h^1 O^1 O_h^1$	none	none	$T_h^1 O^1 O_h^1$
6–3	$T^1 T_h^1 T_d^1$, $O^1 O_h^1$	$T^1 T_d^1$	none	none
4–3–1–1	$T^1 T_d^1$	none	none	none
4–4–1	$T^1 T_d^1$	none	none	$T^1 T_d^1$

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[4] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Pub. No. 18, Carnegie Inst. of Wash., 1922, p. 176.

[5] These arrangements are expressed in the code used by Wyckoff, refs. **3** and 4, pp. 103 *et seg.*

doubles this figure. Such a systematic procedure involves a number of duplications, but it was followed rigidly to lessen the chances of error. The total number of possibilities tabulated was about 1500.

TABLE II

SPACE-GROUPS POSSIBLE FOR VARIOUS ARRANGEMENTS OF O WITH COMBINATIONS OF CA AND AL ALREADY FOUND POSSIBLE

Combinations for oxygen	6–8–1	6–6–3	6–4–3–1–1	6–4–4–1	8–3–3–1	4–4–3–3–1
12–6	$T_h^1O^1O_h^1$	$T^1T_h^1T_d^1$ $O^1O_h^1$	$T^1T_d^1$	$T^1T_d^1$	$T_h^1O^1O_h^1$	$T^1T_d^1$
12–4–1–1	none	$T^1T_d^1$	none	none	none	none
12–33	$T_h^1O^1O_h^1$	none	none	$T^1T_d^1$	none	none
8–8–1–1	none	$T_h^1O^1O_h^1$	none	none	none	none
8–6–3–1	$T_h^1O^1O_h^1$	$T_h^1O^1O_h^1$	none	none	none	none
6–6–6	$T_h^1O_h^1O^1$	$T^1T_h^1T_d^1$, $O^1O_h^1$	$T^1T_d^1$	$T^1T_d^1$	$T_h^1O^1O_h^1$	$T^1T_d^1$
6–6–3–3	$T_h^1O^1O_h^1$	none	none	$T^1T_d^1$	none	none
6–4–4–3–1	none	$T^1T_d^1$	none	$T^1T_d^1$	none	none
6–6–4–1–1	none	$T^1T_d^1$	none	none	none	none

There were no possibilities with O at 16–2, 16–1–1, 12–4–2, 8–8–2, 8–6–4, 8–6–2–2, 8–4–4–2, 8–4–4–1–1, 6–6–4–2 or 6–4–3–3–1–1.

It was found possible to eliminate most of these possibilities by a consideration of the packing-sizes of the ions involved and the space available in the unit cell. Ionic dimensions have been published by Bragg[6] and by one of the present authors.[7] According to Bragg the ionic radii are Ca = 2.1 Å., Al = 1.45 Å. and O = 0.6 Å. According to Davey they are Ca = 1.4, Al = 0.9 and O = 1.0 Å. Davey's values were used in this work for two reasons: first, that they give the distance from Al to O in Al_2O_3 as 1.9, in agreement with the published data of Bragg, and second, that they give a smaller total distance for Ca + O and for Ca + Al, so that they tended to retain certain of the possibilities which would have been thrown out on the basis of Bragg's values. Thus any error introduced by our limited knowledge of the packing dimensions of ions was clearly on the safe side. The procedure of finding whether or not space was available in a given configuration was greatly facilitated by drawing each of the arrangements of equivalent positions involved on tracing cloth. In this way any combination of arrangements could be superimposed and viewed against a bright light. In this manner the ions placed along any one dimension of the cube could be picked out readily.

As an example of this procedure, consider the structure in which Ca is at 8c and 1a, Al at 3a and 3b and O at 6a and 12d. This places $^1/_2$ Ca, 1 O and $^1/_2$ Al along half the cube edge. This requires a space of 1.4 + 2.0 + 0.9 = 4.3 Å. where only 3.8 Å. are available. The structure is obviously an impossibility if the ions have anything like the packing

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[6] Bragg, *Phil.* Mag., 40,236 (1920).

[7] Davey, *Phys.* ***Rev.,*** 22, 716 (1923); *Chem.* ***Rev.,***2, 349 (1926); *Gen. Elec.* ***Rev.,*** 29,274 (1926).

radii assigned to them above. In making these eliminations, the packing dimensions assumed for the ions were not regarded as strictly inflexible. No structure was eliminated unless the available distance involved was exceeded by at least 10%. This procedure eliminated all but about 40 of the original 1500 possible structures. It remained to eliminate as many of these as possible on the basis of x-ray evidence. Among the 40 arrangements allowed by the ionic dimensions were a number of duplications, but these were carried through as a check. In general, however, each of these structures actually represents a number of possibilities which cannot be distinguished experimentally because of the similar dimensions and scattering power of Al and O ions. In the present state of our knowledge of diffracting power, we are hardly justified in distinguishing between Alf^{++} and O^{--} on x-ray data alone. It was therefore assumed that interchanging places between the 6 Al ions and 6 of the O ions has no effect on the diffracting power of the crystal planes. Were this assumption not made, the number of structures to receive individual examination would be much larger than forty.

After it had been decided that the unit cell must have a length of 7.624 Å., repeated attempts were made to detect a first-order diffraction from the 1 0 0 planes for d = 7.624 Å. These attempts gave uniformly negative results. This fact served to eliminate a considerable number of otherwise possible structures without an intensity calculation. In accordance with the general practice, the diffracting power of a plane was taken as proportional to the total number of electrons in the ions which were situated in that plane. The diffracting powers of 1 0 0 planes were calculated for all the forty structures. Those whose 2 0 0 planes were obviously too thinly populated with electrons to cut out the first order from d_{100} = 7.624 Å. were discarded. However, because of the lack of definite knowledge of the correct basis for calculating diffracting powers, no structures were discarded on this basis unless the 2 0 0 planes had less than three-fourths the electron population of the 1 0 0 planes. Repeated attempts to find experimental evidence of a second-order diffraction from d_{100} = 7.624 Å. gave negative results. A few additional structures were therefore eliminated because it was inherent in the structure that the ions were distributed in the space between the 1 0 0 and 2 0 0 planes in such a way as unavoidably to produce such a second-order diffraction.

When all possible eliminations had been made by simple inspection of 1 0 0 planes, there remained only 18 structures, of which 9 were duplicates of the other 9. For instance, the structure having Ca at 8c and 1a, Al at 6d and O at 6b and 12d, may be transformed into the structure having Ca at 8c and 1b, Al at 6a and O at 6c and 12e by merely changing the origin of coordinates from a corner of the unit cube to its body-center. From this point on the duplicates were combined, leaving 9 structures for which intensity calculations must be made. In those cases where two arrangements differed only in having one variable parameter more or less (for instance, 12e and 12n), only the more general arrangement was considered. Similarly, the combination of 6b and 6c was used instead of the special case represented by 12f.

In making the intensity calculation the customary assumption was made that the amplitude of the radiation scattered by a given plane is proportional to the electron population of that plane. This population was determined in the usual manner on the basis of $O^{--} = 10$, $Al^{+++} = 10$ and $Ca^{++} = 18$. The resultant amplitude from a given form was taken as the vector sum of the amplitude from the individual coöperating planes. This was determined by the graphical addition of vectors in the same manner as the addition of alternating currents which have a known phase difference.[8] The intensity of the resultant beam was calculated from the formula[9,10]

$$I = R^2 j \left(\frac{d}{n}\right)^m$$

where R is the resultant amplitude, j is the number of families of planes of the form, n is the order of diffraction and d is the fundamental spacing of the form, taking the edge of the unit cube as unity, and regarding the unit cell as being simple cubic. These calculations showed clearly that six of the nine structures are quite incompatible with the x-ray data. For example, the structure with Ca at Sc and la, Al (or O) at 3a and 3b,

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[8] In this connection see A. Schuster, "The Theory of Optics," Chap. 1, Edw. Arnold, London, **1909, 1919,** or any standard book on alternating currents.

[9] Because of our inexact knowledge of diffracting power this equation can be used only to show qualitatively the relative intensities of diffraction. The simpler the plane form to which it is applied the more reliable are the results. It may be used quite successfully for the 1 0 0 planes—and seems to apply for the 1 1 0 planes. For the 1 1 1 planes the packing radii of the ions are so large in comparison with the interplanar spacing that the calculated results can only be depended upon to show that a line is present or absent in the diffraction pattern. There is a tendency to make the diffracted beam of orders higher than the first abnormally weak. For this reason the formula shows whether the second and fourth orders of 1 1 1 are present and whether the first and third orders are absent, but it does not give the relative intensity of the second and fourth orders.

It is well known that certain crystals act as though the resultant amplitude of the diffraction beam depends upon the square-root of the electron population. For this reason attempts were made to repeat the above calculations on this basis. In no case where this was tried were we able to retain a structure which had been rejected in the original calculations.

[10] Bragg uses $m = 2.0$; Wyckoff uses $m = 2.35$; McKeehan uses $m = 3.0$. None of these seem to be entirely satisfactory. Our Table III was calculated using $m = 2$, merely for the sake of convenience in making the large number of calculations required. It is clear that Table III could have been made to show greater apparent agreement by using a different value for m but it does not follow that such a change would have increased the probability of the correctness of our ultimate solution.

O (or Al) at 6d and O at 12d gave a calculated intensity of 380 for the first order of $d_{100} = 7.624$, and 257 for the fourth order, even when such parameters were used as to give the weakest possible first order and the strongest possible fourth order. Since experimentally the first order is absent and the fourth order is strong, this structure is in direct conflict with the experimental data and must be discarded. Similar calculations on the 1 0 0 planes for the rest of the 9 structures eliminated all but three.

In the case of the three remaining structures it was necessary to make intensity calculations for the first four orders of the 1 0 0, 1 1 0 and 1 1 1 planes. These calculations were made for a large number of different values for the variable parameters which were allowed by the space available for the ions, and by the symmetry requirements of the atomic arrangements. The best fit in intensities was found in the structure illustrated in Fig. 1, in which Ca is at 8c and 1a, Al at 3a and 3b and O at 6d and 12f.[11] The calculated intensities are shown in Table III. It will be noted that they indicate the presence of the three faint lines mentioned at the beginning of this article.

TABLE III

CALCULATED AND OBSERVED INTENSITIES FOR THE MOST PROBABLE ARRANGEMENT

Line	Calculated intensity	Observed intensity
100 1st order ($d_{100} = 7.624$)	75	Absent
100 2nd order	0.1	Absent
100 3rd order	14.1	Absent
100 4th order	1750	Strong
110 1st order	26	Absent
110 2nd order	1420	Very, very strong
110 3rd order	80	Very faint
110 4th order	1500	Weak
111 1st order	163[a]	Absent
111 2nd order	1067[a]	Weak
111 3rd order	69[a]	Absent
111 4th order	552[a]	Faint
211 1st order	4754[a]	Weak
211 2nd order	735[a]	Very strong

[a] Note statements in the text as to the weight to be put on numerical results for these planes.

As was mentioned previously, it is not possible to distinguish with certainty between Al and O ions on the basis either of dimensions or of diffracting power. The assignment of certain of the positions in Fig. 1 to Al and of other positions to O was made on the basis of electrostatic considerations. For instance, in Fig. 1 the x-ray data would permit Al to be at 6d and six of the eighteen O at 3a and 3b. However, since there

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[11] The presence of Al at 3a and 3b leaves room for O at 6b and 6c only at a point half-way between 3a and 3b. This changes 6b and 6c into the special case of **12f.**

are O ions at 12f, we would then have five O ions in a row along a direction parallel to the edge of the cube ($d_{100} = 7.624$ Å.). Such an arrangement is highly improbable from electrostatic considerations. Similarly, the Al might have been placed at 6b (or 6c) with the O at 3a, 3b and 6c (or 6b). This also places five O in direct contact with one another, and is therefore a highly improbable structure. Furthermore, there is some theoretical basis for expecting that Al would have a somewhat greater equivalent scattering power than O, especially in the higher orders and from forms of small spacing. If this be true, the Al at 3a and 3b would cause a fainter 1 1 1 second-order diffraction than the calculated value given in Table III. This would give a still better match with the experimental data.

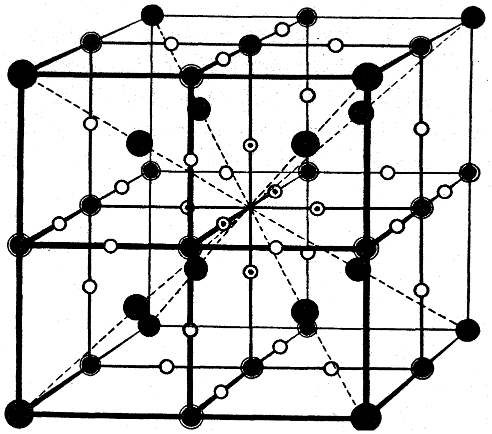
●, Ca; ◉, Al; O, O at 12f; ⊙, O at 6d.

Fig. 1.

It has already been stated that, although the theory of space-groups permits a variable parameter for 12f, the dimensions of Al and O ions fix this parameter in Fig. 1 at $u = 0.25$. Arrangements 6d and 8c have variable parameters. The best intensity match is obtained when u for Ca at 8c = 0.24 and u for O at 6d = 0.31. Intensity calculations show that these parameters are not particularly critical, especially in the case of O at 6d, which may well be somewhat closer to Al at 3a.

The two other structures which were mentioned as possibilities both have Ca at 8c and 1a. One has 6a, 6b, 6c and 6d for Al and O, while the other has them at 6a, 6b, $6b_2$ and 6d. These two structures are closely related, since 6c may be derived from 6b by a single rotation of 90°. While the calculated intensities of these two structures are somewhat less satisfactory than those of the one shown in Fig. 1, the degree of reliability of the laws of scattering with complex crystals is so uncertain that they must be considered as possible structures. In any case, the same general chemical conclusions can be drawn from all three structures.

Chemical Significance **of** the Structure.—It is obvious that there is no particular grouping of ions in any of the three structures of which Fig. 1 is typical. There is no indication of those groups which might have been expected to be present, such as CaO, AlO_3, Al_2O_3, Al_2O_6, etc. The entire structure is built up of Ca, Al and O ions as units. The ionic nature of the compound is evident from its crystal structure. Figure 1 shows **that** the O at 12f are in every case midway between two Al at 3a and 3b, and that each O at 6d is equidistant from four Ca at 8c. Similarly, every Al at 3a is equidistant from each of four O at 12f; every Al at 3b is equidistant from four O at 12f; every Ca at 8c is practically (within 4%) equidistant from six O at 12f, and every Ca at 1a is equidistant from twenty-four O at 12f. Every Al at 3a is equidistant from four Ca at 1a and is equidistant from eight Ca at 8c. Every Al at 3b is equidistant from two Ca at 1a and is also equidistant from eight Ca at 8c. Similarly, every Ca at 1a is equidistant from six Al at 3b and every Ca at 8c is practically equidistant from 3 Al at 3a and from 3 Al at 3b.

Tricalcium aluminate certainly has no grouping which would justify its name. From its crystal structure it would appear to be a mixed oxide and not a salt in any sense of the word. It is distinctly different from solid solutions or mix-crystals, which are either isomorphous substances or simple replacements of one kind of atoms by another kind. In this latter case the structure of one or the other is retained with usually only a change in the lattice dimensions. In the case of tricalcium aluminate the original structure of neither oxide is retained. The structure of tricalcium aluminate is also distinctly different from that of crystals containing complex ions. The complex ionogens whose structures have been determined support the Wernerian conception of secondary valence. $NiCl_2 \cdot 6NH_3$,[12] $K_2Zn(CN)_4$,[13] K_2PtCl_4,[14] $NaClO_3$,[15] etc., are examples of this type of compound. In each of these the complex ion has been found to act crystallographically as a unit, thus confirming the evidence, already strong, from solutions. Tricalcium aluminate, on the other hand, shows the Ca, Al and O to act as crystallographic entities, each surrounded as symmetrically as possible by the other two. In terms of the most probable of the three structures discussed above (see Pig. 1), all six Al ions lie at the intersections of a physical three-dimensional lattice work in such a way as to put an O midway between each pair of Al. This lattice work uses up 12 of the O, so that the lattice work contains two O for every Al. Figure 1 shows, however, that there are no AlO_2 groups existing as physical entities in the crystal. The crystallographic effect might be described as a sort of rectangular sponge of Al and O in the interstices of which are the Ca and the rest of the O ions.

The type of crystal structure reported in this paper for tricalcium aluminate therefore belongs to the fifth type of chemical combination, listed below, *viz.*, (I) ionic compounds (NaCl) (Bragg) in which the crystal is built up of simple ions of an electrolyte; (2) electron-sharing compounds (Al_2O_3) (Bragg) in which the crystal is built up of neutral

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[12] Wyckoff, THIS JOURNAL, **44, 1239 (1922).**

[13] Dickinson, *ibid.*, **44, 276 (1922).**

[14] **Dickinson,** *ibid.*, **44,2404 (1922).**

[15] Dickinson, *ibid.*, **43,2045 (1921).**

molecules; (3) geometrical compounds (Cu_3Au) ($CuAu_3$) (Bain) in which definite proportions are an accident of symmetry in homogeneous atomic dispersions; (4) Wernerian compounds ($CaCl_2I$) (Wyckoff) (K_2PtCl_4) (Dickinson) in which the crystal is built up of both simple and complex ions; (5) mixed ionic compounds ($3CaO \cdot Al_2O_3$).

There remains to be discovered a sixth type,[1] namely, the molecular compound in which molecules of the constituents crystallize together without losing their original identity. As in the case of Type 3, it may be expected that this will be an accidental effect of the symmetry of a homogeneous molecular dispersion of one substance in the other.

Acknowledgments.—It is a pleasure to express our appreciation to the General Electric Company, Schenectady, N. Y., the Calumet Baking Powder Company, Chicago, Ill., and to the Aluminum Company of America, New Kensington, Pa., for placing at our disposal facilities without which this research would have been exceedingly difficult, if not impossible; and to Dr. E. A. Harrington, who first showed that the x-ray diffraction pattern of an impure tricalcium aluminate contained lines corresponding to those from a body-centered cube.

Summary

1. The most probable crystal structure of tricalcium aluminate has been determined and the alternate possibilities stated.

2. The structure of tricalcium aluminate has been shown to be mixed ionic.

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

THE THEORETICAL EVALUATION OF THE ENTROPIES OF AQUEOUS IONS

BY WENDELL M. LATIMER AND CHARLES KASPER

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It has been suggested by Latimer and Buffington[1] that the entropy change, AS, for the process

$$\text{Ion (gas)} = \text{Ion (aq.)}$$

is a function of the charge, e, on the ion, and the radius, r, of the ion cavity in the water solution; AS = $f(e^2/r)$. This relation was noted from an inspection of the experimental values of the entropies of solution and was stated in the form of an empirical equation. The theoretical evaluation of this function will be considered in this article.

The total entropy of hydration may be considered as due to two effects: $\Delta S_{(1)}$, the entropy change arising from the polarizability of the medium,

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[1] Latimer and Buffington, THIS JOURNAL, 48, 2297 (1926).

and $\Delta S_{(2)}$, the entropy change due to the compression of the water, arising from the electrostatic attraction of the water molecules.

The first effect can be obtained by considering the temperature coefficient of the free energy of the process of charging the ion in the gas and water phases. For this free energy, we have the expression first set forth by Born[2] and Fajans[3] and later developed in the works of Hückel,[4] Zwicky[5] and Webb.[6]

The original Born work, which of late has been supported (in so far as the dielectric constant is concerned) by Latimer,[7] Scatchard[8] and Bjerrum,[9] takes the ordinary dielectric constant to be operative. Hückel advanced the idea that the effective dielectric constant must be less than that of pure water in accounting for the course of the activity–coefficient curve. Webb actually succeeded in calculating such an effective dielectric constant, but, unfortunately, the method which involves the selection of an effective moment, and the application of the Langevin theory to water as a normal liquid is open to serious question, especially in the case of entropies.

It is interesting, nevertheless, to see what result the old picture gives us. Thus, using the Born expression

$$\Delta F_{(1)} = -\frac{e^2}{2r}\left(1 - \frac{1}{D}\right) \tag{1}$$

and by differentiation

$$\Delta S_{(1)} = \frac{e^2}{2rD^2}\left(\frac{\mathrm{d}D}{\mathrm{d}T}\right)_P = \frac{-\Delta F_{(1)}}{D^2}\left(\frac{\mathrm{d}D}{\mathrm{d}T}\right)_P\left(\frac{1}{1-\frac{1}{D}}\right) \tag{2}$$

From Kockel,[10] for 25°, the dielectric constant of water is 78; its temperature coefficient is equal to —0.4. Placing these values in Equation 2 we obtain $\Delta S_{(1)} = 6.3 \times 10^{-5}\, \Delta F_{(1)}$ cal. per degree per mole. The magnitude of this quantity is about half that found experimentally for the total entropy of hydration. However, we cannot attach much significance to the numerical result as the temperature coefficient of the dielectric constant of pure water may not be even of the same order of magnitude as that for water under the enormous electrical field about the ion. From

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[2] Born, Z. *Physik*, 1, 4 (1920).

[3] Fajans, *Ber. physik. Ges.*, 21, 549, 709 (1919).

[4] Huckel, *Physik. Z.*, 26, 93 (1925).

[5] Zwicky, *ibid.*, 26, 664 (1926); *Proc. Nat. Acad.*, 12, 86 (1926).

[6] Webb, THIS JOURNAL, 48, 2589 (1926).

[7] Latimer, *ibid.*, 48, 1234 (1926).

[8] Scatchard, *Trans. Faraday Soc.*, 23, 454 (1927); *Trans. Am. Electrochem. Soc.*, 51, 13 (1927).

[9] Bjerrum and Larsson, *Z. physik. Chem.*, 127, 358 (1927); Bjerrum, *Trans. Faraday Soc.*, 23, 434 (1927).

[10] Kockel, *Ann. Physik*, 77, 417 (1925).

the calculations which we are to make it appears that $\Delta S_{(1)}$ must in reality be small in comparison with the other effect. This failure of Equation 2 will be considered in a later paragraph.

The second entropy change accompanying hydration, that is, the change of entropy of the water with pressure, is given by the thermodynamic expression $dS = -(dV/dT)_P dP$. For a differential unit of volume the entropy change is obtained by integrating this expression with respect to the pressure. The total entropy change about the ion is then given by integrating over the total volume of the water outside the ion cavity. Expressing volume as a function of the radius, we obtain

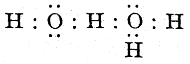
$$\Delta S_{(2)} = -\int_r^\infty \int_1^P \frac{1}{V^0}\left(\frac{dV}{dT}\right)_P dP\; 4\pi r^2 dr \qquad (3)$$

From considerations similar to those of Lorentz for the force density in a polarizable medium in an electric field, Zwicky[5] has developed an expression for the pressure at a distance, r, from a charge, e. The value of this expression depends upon the polarization of the medium by the field. For small fields the polarization is proportional to the field strength and the expression becomes

$$P = \frac{(3 + 2D)\,(D - 1)}{40\pi D^2}\,\frac{e^2}{r^4} \qquad (4)$$

The deviation of the actual pressure at very high values from that given by this expression, due to the electrical saturation of the water, is a matter of some conjecture. The dielectric constant of water may be considered as the sum of three effects: (1) the electronic displacement—this factor is given by the classical relation between the index of refraction and the dielectric constant; (2) the ionic displacements, that is, the stretching of the molecule with respect to hydrogen and hydroxide ions; **(3)** the orientation of the water molecules in the electric field due to their permanent electrical moment. The value of $D_{(1)}$ is about **3** and it has been generally assumed that $D_{(3)}$ is very much larger than $D_{(2)}$ so that the problem may be treated by the methods developed by Langevin.[11] Now, although liquids undoubtedly do exist normally (or under special conditions) in the form of dipoles, we doubt very much whether this is true with associated liquids. Furthermore, it is well known that the theory does not give the correct temperature variation.

Latimer and Rodebush[12] in their discussion of associated liquids have suggested that the association is through "hydrogen bonds," e. g.,



$$\mathrm{H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H:\underset{\underset{H}{\cdot\cdot}}{\overset{\overset{H}{\cdot\cdot}}{O}}:H}$$

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[11] See Webb, ref. 6, and Debye "Marx Handbuch der Radiologie," Akademische Verlagsgesellschaft, Leipzig, Germany, 1925, Vol. 6, p. 618.

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

and that the high dielectric is due to the displacement of the hydrogen held between the oxygen by forces which may, as an approximation, be proportional to the displacement over a considerable distance.

On the basis of either picture, a saturation effect is obtained at high field strengths. With the Langevin theory this would correspond to all of the dipoles being lined up. The other view corresponds to the complete break of the water molecule into hydroxyl and hydrogen ions and this is, of course, what actually happens with ions of sufficiently high field strength, *i. e.*, the ion is hydrolyzed.

However, considering the uncertain nature of these theories, we do not feel justified in attempting to calculate a saturation limit for water. Moreover, we are inclined to believe that the electrical polarization can be taken approximately proportional to the field strength to greater values of the latter than has generally been assumed. For this reason we will use Equation 4, which should hold as a rough approximate for the larger ions. For water at 25° this gives

$$P = 375{,}000\,\frac{e^2}{\text{[illegible]}}\ \text{kg/cm.}^2 \qquad (5)$$

where e is the charge in Faradays (i.e., valence) on the ion and r is expressed in Angstroms.

Large Positive Ions.—To integrate Equation **3** it is necessary to know the coefficient of expansion of water as a function of pressure. This has been determined by Bridgman[13] up to 1000 atmospheres. In order to avoid the problem of extrapolating his data to enormously higher pressures, we shall first consider the case of the larger ions. Using his average value for the coefficient $\frac{1}{V^0}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)$ as 3.2×10^{-4}, we obtain upon integrating Equation **3,** employing also Equation 5

$$\Delta S_{(2)} = -22\,\frac{e^2}{\text{[illegible]}}\ \text{cal. per degree per mole} \qquad (6)$$

To evaluate this entropy change for any ion, we must know the radius of the ion cavity in the water solution. To obtain this we will employ the Born expression, Equation 1, and the experimental values for the free energy of solution, although in doing this we realize that the Born expression is not exact, since it does not include changes in thermal energy and the compression of the water, both quantities, however, being comparatively small, less than 10% for large ions.[14] It must be kept in

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[13] Bridgman, *Proc. Am. Acad. Arts Sci.*, *48*, 300 (1913).

[14] See Webb, ref. 6. Bjerrum, ref. 9, has also considered specific effects which he has treated from the standpoint of the free energy of solution of the discharged ion or corresponding rare gas. The Born expression, since it does not consider the thermal energy, is for a sort of hypothetical absolute zero and therefore is both ΔF and ΔH for the process considered.

It should also be noted that the close agreement of the radius of the ion cavity with mind, moreover, that the dielectric constant in this expression is the "effective" value, but since it is the quantity $(1 - 1/D)$ which is involved, the value of the radius is changed but slightly unless the dielectric constant becomes extremely small, a condition which certainly is not the case for the large ions.

To obtain the free energy values, a revision has been made in energy values calculated by Latimer,[7] *i. e.*, the ΔE values have been converted to ΔF. Account has also been taken, of the association of sodium and potassium into Na_2 and K_2. The values obtained agree approximately with the calculations of Webb.[6]

The experimental entropies of the ions in terms of the entropy of H^+ as zero are those given by Latimer and Buffington.[1] These relative values have been converted to absolute entropies using Eastman's[15] value for chloride ion in 0.01 M solution, 28.0 at 15°. Estimating $\bar{c}_p$ as -12.0,[16] we obtain for the hypothetical 1 M solution at 25° $S_{Cl^-} = 18.3$.

The entropies have then been calculated for the concentration corresponding to the molal gas volume at 25° and 1 atmosphere, *i. e.*, $^1/_{24.4}$ M, to eliminate any entropy change arising from a change in volume upon solution. Finally, ΔS of solution of the gas ion is obtained by subtracting the entropy of the ion as a monatomic gas as given by the Sackur equation.[17]

The data employed and the results are summarized in Table I.

TABLE I

SUMMARY OF DATA USED IN CALCULATING THE ΔS OF SOLUTION AT 25°. ΔF IN *k* CAL. AND ΔS IN CAL./DEG.

	ΔF of soln.	Radius in A.	S of ion, 1 M soln. $S_{H^+} = 0$	Absolute S in 1 M soln.	S in 1/24.4 M soln.	S of gas ion	$-\Delta S$ of solution	
							Exp.	Eq. 3
Na^+	−100	1.64	15	13	20	35.1	15	13.5
K^+	−81	2.03	22	20	26	36.6	10.6	11
Rb'	−78	2.10	25	23	29	39.0	10	10.5
Ag^+	−111	1.52	16	14	20.4	39.7	19	14.5
Tl^+	−79	2.06	26.5	24.5	30.5	41.5	11	10.7
Ba^{++}	−307	2.13	4	0	6	40.4	34	40

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the old values of Bragg for the radius of the positive ions in crystals is entirely accidental and that the latter are actually considerably smaller (about 0.7 Å.). See Pauling, THIS JOURNAL, 49, 765 (1927).

It is, of course, more reasonable to expect that the size of the ion cavity in water would be somewhat greater, and the really important fact remains that the relative size of the positive ions in crystals and in solutions is approximately the same. It may also be that the Born expression gives the radius as the distance from the center of the ion to the center of the water dipole, *i. e.*, the radius of the ion plus the radius of an oxygen ion.

[15] Eastman, THIS JOURNAL, 50, 292 (1928).

[16] Based on the work of Randall and Rossini, unpublished.

[17] See Lewis, Gibson and Latimer, THIS JOURNAL, 44, 1008 (1922).

A comparison of the last two columns of Table I shows an excellent agreement between the experimental entropies of solution and those calculated from Equation 3. If these calculations are correct, we must conclude that the entropy of hydration results largely from the change of ,entropy of the water about the ion due to compression, and that $\Delta S_{(1)}$, the dielectric effect, is small. This may be interpreted as meaning that there is but small entropy change in the orientation of electric dipoles, but a large effect in the loss of thermal energy of the compressed (or tied up) water molecules. This is, of course, just the opposite to the magnitude of these two effects in the free energy of hydration.

The reasons for the failure of Equation 2 are not entirely clear. In addition to the uncertainty regarding the temperature coefficient of the dielectric constant of water under high electric fields, it may also be pointed out that the validity of the equation assumes the constancy with temperature of the radius of the ion cavity. Moreover, it must be kept in mind that the Born expression gives a sort of hypothetical free energy (cf. note, ref. 14) which agrees closely with the experimental value only because the magnitude of the entropy factor is small in comparison.

For the large ions Equations 6 and 1 may be combined to give

$$\Delta S = 1.35 \times 10^{-4} \Delta F \text{ cal./deg.} \tag{7}$$

This is the approximate straight-line relation pointed out by Latimer and Buffington.[1]

Small Ions.—Equation 6, when applied to the smaller ions or to the large ions of higher valence, leads to values which are too high, indicating that at very high pressures the coefficient of expansion of water must be very much smaller. This effect may be noted for Ba^{++} listed in Table I. The theorem proposed by G. N. Lewis[18] that at infinite pressure the entropy of a substance is zero (**i.**e., the integral $\int_1^\infty \left(\frac{dV}{dT}\right)_P dP$ must be equal to the entropy of water at 25°) might be used to extrapolate the coefficient to high pressures. However, the uncertainty in the shape of the curve appears to render it inadvisable to attempt these calculations at this time.

Large Negative Ions.—The entropies of solution of the negative ions have not been included in Table I because of the uncertainties regarding the electron affinities of these ions. If the values for entropies were of somewhat higher accuracy, the calculation might be reversed and Equation 7 used to calculate ΔF of solution and from this the electron affinities. However, it does seem worth while to show that the electron affinities of chloride, bromide and iodide, as calculated from the crystal lattice energies,[19]

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[18] G. N. Lewis, Z. *physik.* Chem., 130, 532 (1927).

[19] Or the values of Angerer and Müller from absorption spectra of the alkali halides, which are in approximate agreement. See Franck and Jordan, "Anregung von Quantensprungen durch Stosse," Springer, Berlin, 1926.

lead to calculated entropy values in approximate agreement with the experimental. The data are summarized in Table II. The entropies of chloride, bromide and iodide are also from the paper by Latimer and Buffington, but instead of taking the values in agreement with the halogen acids, these values have been averaged with those obtained from the silver, thallous and lead salts. The resultant change is, however, small.

TABLE II

SUMMARY OF DATA

	$^1/_2$ X? = $X_{(g)}$ ΔF	+ $^1/_2 X_2$ $E^-_{(g)}$ = $X^-_{(aq.)}$ ΔF	Electron affinity	A F of soln.	S, 1 M X^- $S_{H^+} = 0$	Absolute S 1/24.4 M X^-	S of $X^-_{(g)}$	$-\Delta S$	
								Exp.	Eq. 3
Cl⁻	32	−132	86	78	16.5	24.7	36.4	11.7	10.8
Br⁻	18	−126	86	58	21.8	30.0	38.8	8.8	8.1
I⁻	21	−112	79	54	26.5	34.7	40.2	5.5	7.5

The agreement between the calculated and experimental entropies of solution is probably within the accuracy with which the latter are known and may be considered as substantiating the electron affinities. At the same time, the reasonableness of the result further confirms our theoretical calculation of the entropies of hydration.

These calculations constitute an independent check upon the theory which considers the properties of solutions of strong electrolytes as due to the effect of an electrostatic charge located at the center of a cavity in the dielectric medium. The results seem especially significant in view of the fundamental nature of the ionic entropies and the fact that both the relative and absolute entropies are singularly free from large experimental uncertainties.

Summary

Calculations have been made which indicate that the entropy of hydration of aqueous ions arises largely from the enormous pressures developed about the ion and the resulting decrease in the entropy of the water due to compression.

The entropies of solution of the halide ions are shown to be in agreement with the estimated electron affinities of these elements.

BERKELEY, CALIFORNIA

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

THE HEAT CAPACITY OF OXYGEN FROM 12°K. TO ITS BOILING POINT AND ITS HEAT OF VAPORIZATION. THE ENTROPY FROM SPECTROSCOPIC DATA

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The investigation reported in this paper concerns the entropy of oxygen. Aside from its importance as an element, oxygen is particularly interesting in that its three known crystalline forms, as well as the liquid and the gaseous states, are strongly paramagnetic. The main interest lies in the magnetic behavior of the gaseous state and that of the crystalline state stable below 23.66°K. The fact that the gas has a positive magnetic susceptibility indicates a multiplicity in the quantum states which would lead to a considerable effect in the entropy. The paramagnetism of the solid state suggests the possibility that the application of the third law of thermodynamics in the ordinary manner to the calorimetric data of oxygen may not include a contribution to the entropy[1] arising from a random distribution of magnetons in the solid state. It may be said in advance that this latter effect does not contribute appreciably to the entropy of solid oxygen at the temperatures of liquid hydrogen. This is in rather sharp distinction to the case of $Gd_2(SO_4)_3 \cdot 8H_2O$, where the experimental data show[1c] that the magnetons are contributing over eight cal. per deg. per mole to the entropy of this substance at a temperature of 1.3°K.

The experimental procedure is based upon a calorimetric investigation of the various forms of oxygen from a temperature of 11.75°K. to the gaseous state at the boiling point. From the measurements the entropy of oxygen was calculated and found to be in agreement with that calculated from spectroscopic data. The purpose necessitated the attainment of high accuracy in the calorimetric measurements.

Preparation and Purification of the Oxygen

The oxygen was prepared by electrolysis of a sodium hydroxide solution in an electrolytic cell which operated on a current of four hundred amperes. Although generated in a commercial cell, there was little reason to expect impurities other than hydrogen and ozone since the electrolyte in the cell had been in service for a number of years (sufficient to bring about the removal of objectional impurities, if any) and was protected from contact with the air. From the generator the oxygen was carried under pressure to the purifying train. Special high vacuum stopcocks were employed and these were greased with rubber stopcock grease previously saturated with oxygen gas at 150°. Before use the entire purifying train was tested and found to hold a vacuum of 10^{-5} mm. of mercury. Adsorbed gases were removed by warming and sparking the glass

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[1] (a) Schottky, *Physik. Z.*, 22, 1 (1921); (b) **23**, 9 (1922); (c) Giauque, THIS JOURNAL, 49, 1870 (1927).

line a number of times and by evacuating it over a period of several days. Finally, a continuous stream of oxygen gas was passed through the line for several hours before any was collected. The train consisted of a tower of potassium hydroxide sticks to remove moisture, a long column of oxidized copper turnings heated to 400° in an electric furnace to remove hydrogen, two more towers of potassium hydroxide sticks, a tube filled with amalgamated copper turnings to decompose ozone (the potassium hydroxide and the copper oxide are also catalytic agents in the decomposition of ozone), two meters of tubing packed alternately with plugs of glass wool and of phosphorus pentoxide, and several bulbs, for use in fractionally distilling the liquid. We relied on the fractionation as the most reliable portion of the process for the removal of the final traces of impurity. The liquid oxygen was subjected to four steps in the fractionation. In each step only the middle portion was saved. About **600** cc. of liquid oxygen initially collected was reduced to a little over **100** cc. of final product which was distilled into the calorimeter. Before heat capacity measurements were begun, the oxygen in the calorimeter, frozen by the aid of liquid hydrogen, was evacuated with a mercury vapor pump for an hour or so to remove any last trace of hydrogen. Kahlbaum's phosphorus pentoxide was employed and Baker and Adamson's C. P. potassium hydroxide as reagents.

This method of purification is substantially that followed by Baxter and Starkweather[2] in their precise density determinations. We are using their value for the density of oxygen. We made no analysis of the oxygen; however, the shape of the heat capacity curve below the melting point and the sharpness of the melting point temperatures showed qualitatively that the oxygen was very pure. Oxygen was prepared on five different occasions. The various preparations of oxygen will be referred to by the designations I, II, III, IV and V.

Experimental Procedure

The experimental procedure in measuring heat capacities and in working up the data corresponded in the main to that of Giauque and Wiebe[3] in their measurements on the halogen acids and we employed the same gold calorimeter, II, and other portions of the same apparatus employed by them. The essential features of the method consisted in introducing a measured amount of heat electrically to the substance contained in the vacuum-jacketed calorimeter and measuring the temperature rise on a sensitive gold resistance thermometer calibrated at frequent intervals against a standard thermocouple soldered to the bottom of the calorimeter. The methods differed in certain important respects from those of Giauque and Wiebe. We will briefly outline some of these changes.

Timing.—To replace stop-watch and hand control of the electrical energy input circuits, a timing mechanism[4] that opened and closed the circuits electrically in response to time signals was designed. The time signals were obtained through the courtesy of the Astronomy Department of the University of California. By calibration it was shown that the heating intervals were thus timed within a maximum limit of error of 3×10^{-3} seconds in an absolute sense, which affected the final heat capacity values in the most unfavorable circumstances by only one part per hundred thousand. Measurements were made with sidereal time but this was corrected to solar time by the equation 1 solar second = **1.002738** sidereal seconds.

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[2] Baxter and Starkweather, *Proc. Nat. Acad. Sci., 12,* 699 (1926).

[3] Giauque and Wiebe, THIS JOURNAL, **50,101** (1928).

[4] Johnston, **J.** *Opt. Soc.* **Am., 17, 381** (1928).

Amount of Material Present in the Calorimeter.—The apparatus for measuring the amount of material present in the calorimeter during heat capacity measurements is shown in Fig. 1. The measuring bulb **A** is made from a five-liter pyrex round-bottomed flask and is supported in the hemispherical casting B. The internal diameter of B is a half inch larger than the external diameter of **A** and the intervening space is filled with a cast of Woods metal, C, poured when **A** was clamped in position. To the top and bottom of **A** are fused the small-diameter glass tubes D and E which bear etched scales marking volume intervals of 0.1 cc. The volume included between these two scales was determined by two calibrations which gave agreement to 0.13 cc. The calibrations were made by weighing mercury. The usual precautions in exact volume calibration were taken and the small volume effect due to distortion of the bulb by mercury pressure was evaluated. After calibration the lower end, E, was fused to a glass tube extending to the bottom of the six-liter cast-iron mercury reservoir F. This whole apparatus was immersed in a 25° thermostat which maintained a temperature constant to 0.01°.

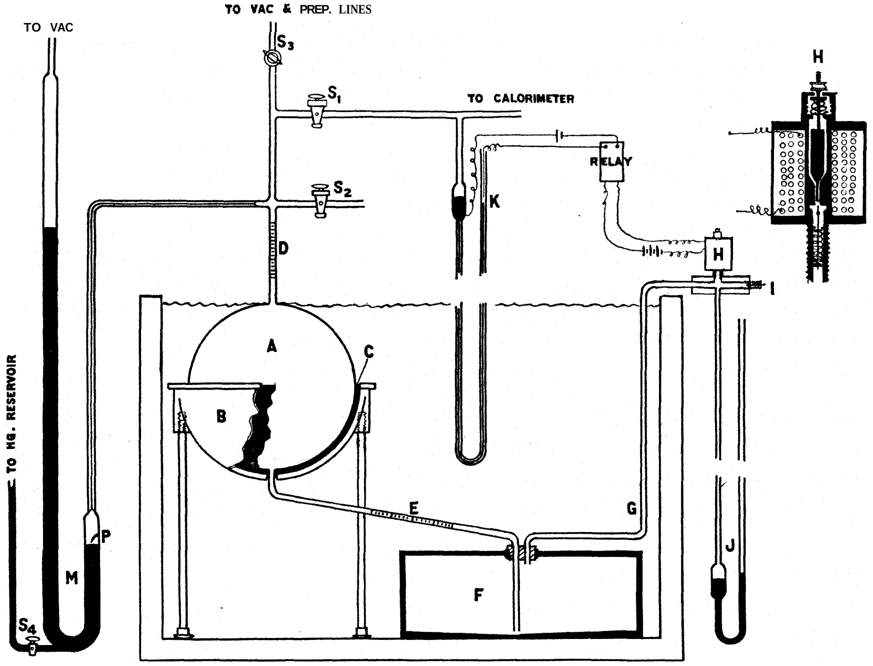

Fig. 1.

When the heat capacity measurements were completed and it was desired to measure the amount of substance present in the calorimeter, pressure was applied through the bicycle valve I to force mercury into Bulb **A**. A portion of the substance in the calorimeter was then vaporized by supplying heat and gas was collected in the bulb **A**. At the same time pressure was released in F by action of the electromagnetic valve H, whose action is described more fully in the next title, so that the mercury returned to the reservoir and the gas collected in **A** at atmospheric pressure. When **A** was almost filled with gas, as evidenced by the mercury height in the capillary manometer J, which was calibrated against an empirical scale, the vaporization was stopped and S_1 was closed. Further pressure was released in F by hand manipulation of the valves and the mercury meniscus was brought into the lower scale E. The pressure was then read on the constant dead-space, large-diameter manometer M which was enclosed in an air-jacketed case and was connected to A through capillary tubing to diminish volume external to the thermostat. The pressure was read with the aid of a standard meter scale and a Société Génévoise Cathetometer. This process was repeated until all of the material in the calorimeter was vaporized. It ordinarily required about eighteen repetitions to complete the measurement. These measurements included a small amount of gas in the line external to the thermostat. Although neither volume nor temperature of this portion of the gas was known to the same accuracy as that enclosed in the thermostat, the amount was small compared to that in A; moreover, it was largely canceled out since ordinarily gas at nearly the same pressure occupied this space both before A was filled with gas and after. The final of the 18-odd measurements included gas in the entire line volume, including the calorimeter. The calorimeter was warmed up to room temperature before this final measurement and it was usually possible to arrange that this should be a measurement of gas at low pressure so that the uncertainty of this volume introduced a negligible uncertainty into the total amount.

The following equation was employed for calculating the amount of gas from the PVT relationship.

$$\text{Amount in moles} = V{\cdot}P{\cdot}\frac{d}{M}\cdot\frac{1}{1+kT}\cdot[1+\alpha\,(1-P)]$$

where V = volume in liters, P = pressure in international atmospheres, d = density of the gas per liter at standard conditions, M = molecular weight, k = mean coefficient of thermal expansion for the range from 0 to 25°, T = temperature in °C. and α = the coefficient of deviation from Boyle's Law per atmosphere. In deriving P from the measured pressure, corrections were applied as given in "International Critical Tables,"[5] for temperature of mercury and of the standard meter scale and for capillary depression as measured by meniscus height. The gravitational acceleration was taken as 979.973 cm./sec.^{2} as given by Sternwarte[6] for this locality. The values used for the remaining constants employed in this equation are as follows: d = 1.42898,[2] k = 0.003672,[7] $\alpha = -0.00087$.[8] Any error in these constants will, of course, affect all of the heat capacity determinations alike. However, the uncertainty in these constants is so small that error from this source may be neglected.

Measurements of Heat of Vaporization

The heat of vaporization was measured by what corresponds to Method II in the paper of Giauque and Wiebe. The absorption bulb of their measurements was necessarily replaced in this work by the measuring bulb A described under the previous heading and the heating interval was chosen of such a length as not quite to fill the bulb.

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[5] "International Critical Tables," McGraw-Hill Book Co., New York, 1926, Vol. I.

[6] Landolt, Bornstein and Roth, "Physikalisch-Chemische Tabellen," Berlin, 1923.

[7] We used the value employed by Baxter and Starkweather. This is close to the value (0.003674) obtained by Jolly, *Pogg. Ann.*, Jubelband, 96 (1874).

[8] Batuecas, Maverick and Schlatter, *J. chim. phys.*, 22, 131 (1925).

The automatic pressure control by the electromagnetic valve H maintained a pressure constant to about 0.1 mm. of mercury during the measurement. This resulted in constancy of temperature and consequently of resistance in the combined resistance thermometer heater by which the energy was supplied to the calorimeter. A very constant energy current was thus maintained and it was possible to read this factor with great accuracy in the course of the measurements. The construction of H is shown more clearly in the inset to the right of the diagram of Fig. 1. The basic ideas in the construction of this valve and in the electrical set-up are due to Smith.[9] When the pressure registered in the line leading from the calorimeter exceeds a certain predetermined value, an electrical circuit is completed through contact of the mercury with a platinum wire at K. Through a relay this energizes the magnet at H whose armature depresses the stem of a bicycle valve and releases air pressure from the reservoir F. This causes mercury to flow from A and lowers the line pressure. With proper adjustment at H, the regulator can be made very sensitive. The contact at K was adjustable and by this device heats of vaporization could be measured at any desired pressure. However, in this research, all measurements were made at a pressure of 760 mm. of mercury.

Attainment of Low Temperature.—Low temperatures were obtained by liquefaction of hydrogen and subsequent evaporation at low pressures in the manner of Giauque and Wiebe[10] but between the calorimetric apparatus and the vacuum pump of 150 cubic feet displacement mentioned in their article, a battery of three large Nelson oil vacuum pumps connected in parallel was included. These had a total displacement of 12 cubic feet per minute and were capable of producing a vacuum of better than 10^{-3} mm. of mercury in a non-gassing system. With their aid, a maximum temperature lowering to 10.7°K. was produced, although no heat capacity measurements were begun below about 11.7°K. The accuracy of the low temperature measurements was improved by breaking the vacuum in the space surrounding the calorimeter while cooling down, by use of helium gas at low pressure in preference to hydrogen gas. The helium was adsorbed to a much smaller degree than was the hydrogen and it was thus possible to regain a high vacuum in a much shorter interval following the cooling and to operate with a greatly reduced heat leak during the early measurements.

Temperature Scale.—The temperature intervals in the heat capacity measurements were determined from readings of a gold resistance thermometer wound on the exterior surface of the calorimeter and calibrated at short intervals in the course of heat capacity measurements by comparison with a standard copper constantan thermocouple W soldered to the bottom of the calorimeter. The method of treating the calibration data was that described by Giauque and Wiebe. The temperature scale for thermocouple W was fixed in terms of the hydrogen gas thermometer by Giauque, Buffington and Schulze,[11] and in terms of the hydrogen vapor pressure thermometer by Giauque, Johnston and Kelley,[12] for which it was the direct standard of comparison. These authors also found it in agreement with the oxygen vapor pressure thermometer. In the course of the heat capacity measurements, it was again compared with the oxygen vapor pressure thermometer and found to be in agreement and at the end of the measurements it was compared a second time with the hydrogen vapor pressure thermometer and found in agreement. The temperatures given by thermocouple W are believed to be correct to within 0.05". All fixed temperature points recorded in the data that follow, such as transition points, melting points and boiling and vapor pressure points, are based directly on the temperature readings of thermocouple W. The readings taken from the resistance

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[9] Smith, *Ind.* Eng. *Chem.*, **16**, 22 (1924).

[10] Cf. Latimer, Buffington and Hoenshel, THIS JOURNAL, 47, 1571 (1925).

[11] Giauque, Buffington and Schulze, *ibid.*, 49, 2343 (1927).

[12] Giauque, Johnston and Kelley, ibid., 49, 2367 (1927).

thermometer should represent the temperature intervals correctly to within 0.001 to 0.003' since over a short interval the absolute error of calibration should not vary appreciably and since the resistance readings are reproducible to 0.001 ohm, which corresponds to 0.001° over nearly the entire temperature range above 35°K. At lower temperatures, errors in the temperature interval may be larger and may approximate 0.01 to 0.05' at the very lowest temperatures, where dR/dT rapidly diminishes. Two different resistance thermometers of nearly similar character and dimensions were employed in the course of the measurements.

Corrections to the Experimental Data. - In addition to corrections involving only physical constants of the substances measured, the following experimental corrections were applied because of conditions peculiar to the method and apparatus.

(a) A correction amounting normally to about 0.2 of 1% of the total heat input was applied for heat generated in a resistance of 55,000 ohms shunted across the thermometer heater terminals for purposes of measuring the potential drop. This correction could be applied with high accuracy.

(b) A correction was applied for heat generated in a pair of No. 40 copper leads one inch in length bridging the vacuum space surrounding the calorimeter and connecting the gold resistance thermometer ends with the so-called thermometer terminals which were in thermal contact with the surrounding jacket. It was assumed that half the heat generated in this pair of leads went to the calorimeter and that half was conducted to the surrounding jacket. This entire correction amounts to only about 0.02 of 1% of the total energy.

(c) A correction amounting to 0.2 of 1% at liquid-air temperatures and increasing several fold at lower temperatures was applied for heat interchange between the calorimeter and its surroundings during the heating period. This correction was obtained from measurements of warming rates before and after each run and could be applied with an error not over from 10 to 20% of the correction.

(d) A supplementary correction was applied to make allowance for the temperature head of the resistance thermometer from radiation and conduction during resistance measurements. This correction was evaluated through the application of Newton's Law of Heat Transfer combined with certain assumptions involved in the geometry of the apparatus. It affected the specific heats by less than 0.05 of 1% over the greater portion of the temperature range investigated, and introduced an uncertainty of 0.01 or 0.02% into the final data.

(e) Correction was applied for heat spent in vaporizing material into the 70-odd cc. of line volume adjacent to the calorimeter. This correction was effective over about the last thirty degrees of the heat capacity range investigated. It amounted to about 1% of the total energy input for the heat capacity measurement at the highest temperature, but its importance dwindled rapidly for the measurements at lower temperatures.

The correction itself might be in error by as much as 10%. In applying this correction we used the data of Cath,[13] in agreement with our own[12] for oxygen. Allowance was made for the vapor space within the calorimeter, for which we employed the densities of liquid oxygen given by Mattias and Onnes.[14]

(f) A correction amounting to from 10% to 15% of the total energy supplied was necessary to take account of the heat capacity of the empty calorimeter. This was evaluated from heat capacity measurements carried out on the empty calorimeter with the same care as those carried out on the substances investigated. The heat capacity of the empty calorimeter was determined in three separate series of measurements carried out, respectively, before, during and after the period covered by the measurements. A smooth curve fitted the experimental values to within 0.1 of 1% with almost no exceptions.

In measuring heats of transition, fusion and vaporization the heat interchange correction corresponding to corrections (c) and (d) was applied graphically by plotting, respectively, temperatures of calorimeter and of surrounding jacket against time elapsing during the measurement. From the area between the two curves thus obtained and with the further employment of an empirical heat interchange factor experimentally determined as a function of temperature difference between calorimeter and surroundings, the correction was applied. In one or two instances the magnitude of this correction exceeded 1%. More often it was about 0.2 or 0.3 of 1%. This correction introduced an uncertainty of about 10% of its value.

Probable Errors

Heat Capacity Measurements.—The expression for obtaining the heat capacities from the experimental data takes the form

$$C_p \text{ (at } T) = \frac{\left(\frac{\epsilon \cdot I \cdot t}{\Delta T} \cdot W\right) - C_c}{A}$$

where ϵ = voltage across heater terminals during heat input, I = amperes through heater during heat input, t = the time of heat input in seconds, W = factor for converting joules to calories. This factor is taken from "International Critical Tables."[5]

We express our results in terms of the 15° calories: C_c = heat capacity of the empty calorimeter, A = amount of material present in the calorimeter. By means of a White double potentiometer, ϵ was known to within 0.05 of 1% and I to within 0.02%.

The factor "t" is known with very high accuracy. In the most un-

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[13] **Cath,** *Comm. Phys. Lab. Univ. Leiden,* 152d (1918).

[14] Mattias and Onnes, *ibid.,* 117 (1911).

favorable circumstances, its limit of error has been mentioned as of about 0.001 of 1%.

AT is determined from resistance measurements made with the White potentiometer. As the temperature interval was usually between 4 and 5°, 0.05 of 1% appears a reasonable limit of error in this factor. To this must be added a possible error of 0.1 of 1% for uncertainty of temperature scale on the resistance thermometer. It should be mentioned that this latter error will have little effect on the entropy since if the temperature coefficient of resistance is too high in some temperature region, it must be too low by a corresponding amount in some adjacent temperature region.

The correction for heat capacity of the calorimeter has been discussed under the heading correction (f). The uncertainty present in this factor may introduce an error of from 0.01 to 0.03 of 1% in the final values of C_p.

Error in the amount of material present in the calorimeter is introduced by each of three factors, pressure, volume and temperature of the gas. Prom a consideration of these combined factors, the amount of gas measured cannot be in error by more than 0.03 of 1% for an individual measurement and must average to a somewhat smaller limit over the eighteen-odd measurements involved in obtaining A.

The limits of error present in these factors combined with those introduced in the corrections (a), (b), (c), (d) and (e) thus cannot introduce a greater maximum error than about 0.4 of 1% into individual specific heat points and that only for the highly improbable assumption that all errors are present at a maximum and in the same sign. The probable error should not exceed half of this figure. As a matter of fact C_p values obtained with this apparatus rarely deviate from a smooth curve drawn through the points by over 0.1 of 1% in the region above 35°K.; 0.2 of 1% appears to be a reasonable limit to the error of the smooth curves through our data. The statements here made apply only for the temperature region above 35°K. Below that temperature the inaccuracy increases, due in part to the increase in the relative importance of the various correction factors, to the smaller heat capacities but principally to the decreasing dR/dT of the resistance thermometer. At 20°K. the values for C_p may be as much as 0.7 of 1% in error and at 12° the errors of measurement may be as high as 5%.

Heats of Transition, Fusion and Vaporization.—The heats of transition and fusion contain about the same probable error as do the specific heats. The heats of vaporization are somewhat more accurate, however, due to a smaller contribution from several factors that introduce the major inaccuracies. The more important of these favorable influences are the small, almost negligible, AT; the nearly constant energy current, **I;** the smaller correction for extraneous heat capacity and the smaller inaccuracy remaining in the heat interchange correction. The mean of the several determinations of heats of vaporization is believed to be correct to within 0.1 of 1%.

Heat Capacity Data.--pour series of measurements were carried out to determine the heat capacities of solid and liquid oxygen. Each was carried out with a different lot of oxygen and the preparation numbers corresponding to these four lots will serve to describe the series. Series

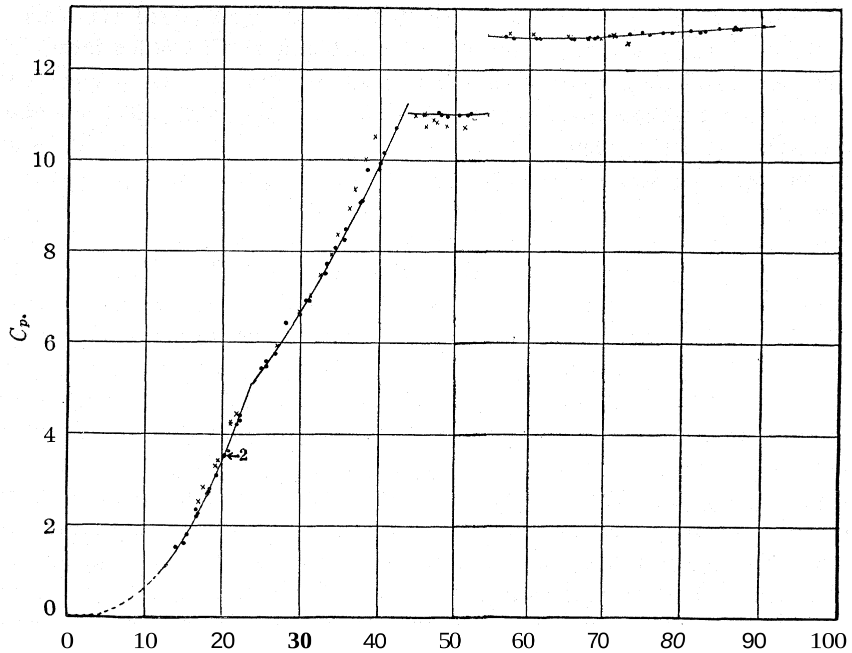
TABLE I

HEAT CAPACITY OF OXYGEN

Molecular weight, 32.000. Series I, 3.8387 moles; Series II, 3.7762 moles; Series IV, 3.9498 moles; Series V, 3.7829 moles.

Series	T, °K.	AT, °K.	C_p/mole in cal./deg.
V	12.97	2.445	1.10
IV	14.14	1.389	1.52
V	15.12	1.685	1.60
IV	15.57	1.323	1.79
II	16.66	1.324	2.33
V	16.80	1.496	2.18
IV	16.94	1.120	2.25
IV	18.13	1.120	2.67
II	18.32	1.604	2.71
V	18.45	1.676	2.79
IV	19.34	1.197	3.07
II	20.26	1.596	3.50
V	20.33	1.923	3.52
IV	20.85	1.494	3.60
II	21.84	1.317	4.20
IV	22.24	1.238	4.27
V	22.24	1.776	4.40
Transition at 23.66°			
IV	25.02	0.905	5.42
II	25.61	1.618	5.57
V	25.61	1.981	5.47
IV	26.75	2.494	5.75
V	28.00	2.781	6.05
II	28.08	2.405	6.42
IV	29.88	3.699	6.61
II	30.63	2.582	6.94
V	31.08	3.260	6.93
IV	33.05	2.580	7.52
II	33.33	2.787	7.73
V	34.41	3.244	8.08
IV	35.57	2.423	8.26
II	35.77	2.290	8.49
V	37.59	3.037	9.08
IV	37.85	2.024	9.12
II	38.47	2.936	9.80
IV	39.99	2.122	9.80
V	40.18	2.090	9.92
II	40.67	1.474	10.16
V	42.21	1.903	10.73
Transition at 43.76'			
IV	45.90	3.825	11.02
II	47.76	2.055	11.07
V	48.11	3.723	11.01
IV	48.97	2.208	10.99
II	50.55	3.152	11.01
V	51.68	3.338	11.03
IV	52.12	3.979	11.06
Melting Point at 54.39°			
V	56.95	3.360	12.76
II	57.95	3.056	12.72
V	60.97	4.596	12.71
II	61.48	3.944	12.71
II	65.57	2.887	12.71
V	65.92	4.282	12.71
I	68.77	3.277	12.73
II	69.12	4.159	12.75
V	70.67	5.104	12.77
I	71.38	3.245	12.78
II	73.31	3.848	12.81
I	74.95	3.767	12.85
V	75.86	5.070	12.80
II	77.58	4.632	12.84
I	78.68	3.640	12.83
V	81.13	5.395	12.88
II	82.31	4.748	12.86
I	82.96	4.681	12.88
I	84.79	3.704	12.93
V	86.43	5.151	12.91
II	86.61	4.619	12.95
II	86.97	4.526	12.92
I	87.32	3.924	12.91
V	90.33	2.612	12.99

I was carried out only for liquid oxygen; Series IV only for solid as a short circuit developed during the heat of fusion determinations. Series II and V covered both solid and liquid. Series V covered the extremes of the temperature interval investigated, as its measurements extended from 11.75°K. to 91.64°K. The individual results are tabulated in Table I. Column 1 gives the series number, Col. 2 the mean absolute temperature, Col. 3 the temperature interval covered and Col. 4 the heat capacity in calories per mole per degree.



Temperature, °K. ●, This Research; X, Eucken.

Fig. 2.—Heat capacity in calories per mole of oxygen.

These data are reproduced graphically in Fig. 2, where the dark circles represent the values obtained in the individual measurements. The various series of measurements are in good agreement for liquid oxygen as only six of the twenty-four measurements secured over that range lie off the smooth curve by more than 0.1 of 1%. The largest deviation is 0.3 of 1%. This curve is believed to represent the correct heat capacity for liquid oxygen to within 0.2 of 1%. The initial downward slope of the curve with a subsequent upward trend may indicate the presence of an equilibrium between polymerized and unpolymerized molecules with small heat of dissociation as predicted by Lewis.[15] This comment

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[15] Lewis, THIS JOURNAL, **46**, 2027 (1924).

is in keeping with the minimum observed in the heat capacity data for water; see, for example, the data given by Barnes.[16]

The same degree of accuracy cannot be claimed for the curves representing the heat capacities of solid oxygen as for the liquid since the various series do not lead to quite the same close agreement, particularly for the two forms stable at lower temperatures. We cannot reconcile this small disagreement with what is believed to be the normal accuracy of the experimental method, particularly since repeated measurements made in determining the heat capacity of the empty calorimeter—an essentially more difficult measurement for the attainment of accuracy—and the various measurements for the liquid and for other substances all yielded individual values in good agreement with the respective curves. We suspect that the somewhat poorer agreement for solid oxygen may be due to some characteristics in its behavior observed by Wahl,[17] who found that liquid oxygen becomes viscous close to its freezing point and readily supercools to a glass interfused with crystals of the solid modification stable just below the melting point. When cooled to the transition (at 43.76°K. by our measurements), Wahl reports that the crystal modification stable below that temperature is formed almost instantaneously from the supercooled glass. This crystal form cracks badly and appears to have a considerably greater density than the higher temperature form. The latter property would lead to poorer thermal conductivity within the calorimeter and would increase the difficulties attendant on the attainment of accuracy. The former property might result in slight differences in physical composition in various instances. The comparative sharpness of transition and melting points discussed in the next section precludes the possibility of our having had more than traces of a physical form other than the respective pure crystals. Lest we convey an exaggerated impression of the irregularities in heat capacity to which we are referring, it should be mentioned that the individual measurements for the various solid modifications seldom were off the curves drawn by more than a very few tenths of one per cent., but the number of points that deviated over wider limits and the average deviations as well were considerably larger than for the other measurements. Due to the large number of points obtained, the curve for Solid I (43.76°K. to the melting point) is believed to be correct to within 0.3 of 1%, that for Solid II (23.66°K. to 43.76°K.) to within 0.5 of 1%, and that for Solid III (below 23.66°K.) to within 1% at its upper extremity but increases in uncertainty with temperature lowering and may be in error by 5% at the lowest temperature the measurements attained. In drawing the curves low weight has been given to certain measurements for which experimental

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[16] *Barnes, Trans. Roy. Soc. London, 199,* 149 (1902).

[17] Wahl, *Proc. Roy. Soc. London,* **88,** 61 (1913).

conditions were less favorable, as shown by entries in the data books, and no weight has been given to two points obtained in Series I for Solid II which we could not substantiate in the later series when special care was given to those particular temperatures.

The graph includes the results of Eucken[18] shown by crosses. For Solid III Eucken is higher than our curve by amounts ranging from 6 to 14%, with an average deviation of 10%. Eucken's results are in agreement with ours for Solid II up to about 34°K. Above this temperature they deviate sharply and at 39°K. are about 9% above the curve. For Solid I Eucken obtains values lower than ours by about 2% on the average. For liquid oxygen the values of Eucken begin about 0.4 of 1% higher and approach the curve. His last point at about **73°K.** is 1% lower than the curve. It seems probable that much of the discrepancy between Eucken's measurements and this investigation is due to his temperature scale between the liquid hydrogen and liquid air regions. It can be noticed that his measurements for Solid I are low and those for Solid II are high. This would be in accord with the fact that he recorded 42.5°K. for the I–II transition against the value of 43.76 ± 0.05°K. This transition temperature is very easily measured.

Melting and Transition Temperature.—The melting point was determined in one series of measurements with Preparation IV. The transition temperatures were both determined with Preparation III.

In determining the melting point the oxygen was first cooled below 40°K. and then warmed through the transition (Solid II to Solid I) in order to avoid the presence of supercooled liquid so far as possible. After warming into the melting point, twelve measurements were taken over a period of sixty-five hours and with different proportions of solid melted. The thermocouple showed an extreme difference of 0.05° and the resistance thermometer, which is essentially the more reproducible of the two, showed a maximum change of 0.015". From these measurements the melting point was selected as 54.39 ± 0.05°K.

In determining the temperature of the higher transition seven measurements were taken over a period of eight hours. The thermocouple showed an extreme variation of 0.04" and the resistance thermometer a variation of 0.015". From these measurements the value 43.76 ± 0.05°K. was obtained.

The lower transition temperature was studied over a period of five hours. Due to the low heat capacities of the portions of the apparatus, the low heat of transition and the difficulty of maintaining adequate constancy in the temperature of the surroundings at this temperature the same constancy of results could not be expected as for the higher temperatures. Both thermocouple and resistance thermometer showed a temperature

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[18] **Eucken,** *Ber. physik. Ges.*, **18,** 4 (1916).

variation of 0.1° among the eleven measurements carried out, in the course of which the percentage of oxygen transformed was increased from about 15% to about 65%. The value was 23.66 ± 0.1°K.

TABLE II

MELTING AND TRANSITION TEMPERATURES OF OXYGEN

Observer	Transition Temp., °K.	Transition Temp, °K.	M. p., °K.
This research	23.66 ± 0.10	43.76 ± 0.05	54.39 ± 0.05
(1916) Eucken[18]	23.5	42.5	54.1
(1911) Onnes and Crommelin[19]	..	..	54.7
(1911) Dewar[20]	..	..	54
(1903) Estreicher[21]	..	..	46

Heats of Fusion and Transition.—The heats of fusion and transition were measured in the usual manner, starting the heat input at a temperature a little below the melting point and ending at a temperature a little above. Correction was applied for $\int C_p dT$. The results are shown in Table III.

TABLE III

HEATS OF FUSION AND TRANSITION OF OXYGEN

Series I, 3.8387 moles; Series II, 3.7762 moles; Series IV, 3.9493 moles; Series V, 3.7929 moles.

Series	Temp. interval	Corr. total heat input (cal.)	$\int C_p dT$	ΔH, cal. per mole	Mean
		Fusion at 54.39'			
II	52.73–56.40	591.84	190.15	106.37	106.3 ± 0.3
V	53.86–55.24	499.20	96.66	106.13	
		Transition at 43.76°			
II	41.78–45.09	827.70	154.40	178.28	
IV	41.12–43.98	836.90	136.48	177.34	177.6 ± 0.5
V	43.20–46.20	814.58	142.09	177.29	
		Transition at 23.66'			
II	22.68–24.65	125.82	41.08	22.44	
IV	22.87–24.55	125.72[a]	36.91	(22.3–22.5)[a]	22.42 ± 0.1
V	23.16–24.60	115.63	30.68	22.40	

[a] Due to partial loss of vacuum during this measurement, a heat interchange correction amounting to one calorie in the total energy was rendered uncertain by 100%. Choosing the extreme limits for the uncertainty of the correction, we get the limiting values of A H included in the table.

Eucken[18] obtained 15.7 and 19.2 in two determinations of the lower transition heat, 166.7 and 168.0 in two determinations of the higher transition heat and 105.5 in one determination of the heat of fusion.

Heat of Vaporization.—The heat of vaporization was measured in the

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[19] Onnes and Crommelin, *Comm. Phys. Lab. Univ. Leiden,* No. 121c (1911).

[20] Dewar, *Proc. Roy. Soc. London,* **85A,** 597 (1911).

[21] Estreicher, Bull. *intern. acad. sci. Cracovie,* 836 (1903).

manner described earlier in this paper. The pressure was maintained constant at 76 cm. of mercury within 0.1 mm. All measurements were made with Preparation I. Heat was supplied for thirty-five minutes in the first measurement and for thirty-seven minutes in those following. The results are shown in Table IV.

TABLE IV

HEAT OF VAPORIZATION OF OXYGEN

Boiling point, 90.13°K.

This research		Other observers	
Moles O_2 evaporated	AH, 760 cm. of Hg in cal./mole	Observer	A H
0.20513	1629.4	(1925) Dana[z2]	1631.7[b]
.20944	1627.8	(1916) Eucken[18]	1600"
.20871	1629.2	(1914) Keesom[23]	1625
.20714	(1635.4)"	(1911) Barschall[24]	1641
.20808	1629.2	(1906) Alt[25]	1629
.20688	1628.5	(1906) Dewar[26]	1635
Value chosen, 1628.8 ± 1.6		(1904) Estreicher[27]	1850
		(1903) Shearer28	1905

[a] The value in parentheses was given no weight in arriving at this value.

[b] This is a mean of 24 determinations varying from 1629.9 to 1638.5. 0.2 of 1% (3.3 calories) is claimed as the limit of error for the mean. We have corrected Dana's values to the "International Critical Tables" value for the mechanical equivalent of heat and to Baxter and Starkweather's value for the density of oxygen to correspond to the present work.

[c] Eucken states that on account of his experimental procedure, his heat of vaporization probably corresponds to a pressure higher than atmospheric.

Entropy from the Heat Capacity Data.—We have calculated the entropy of oxygen gas at the boiling point of oxygen, making use of the heat capacity data. In making the extrapolation below 11.75°K. the Debye function with $\beta\nu = 90.9$ has been used. It has been assumed that the oxygen molecule is acting as a unit at these low temperatures. The extrapolated entropy of 0.32 entropy units is very unlikely to contribute an appreciable error. Lewis and Gibson[z9] made a similar calculation from the data of Eucken.[18] In Table V is summarized the entropy contribution of the various $\int C_p d \ln T$'s and ΔH's, both from our own data and from those of Eucken. The temperatures recorded in the first column are the present transition, melting and boiling point values. The entropy

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[22] Dana, *Proc. Am. Acad. Arts. Sci.*, *60*, 241 (1925).

[23] Keesom, *Comm. Phys. Lab. Univ. Leiden,* 137e (1914).

[24] Barschall, *Z. Electrochem.,* 17, 345 (1911).

[25] Alt, *Ann. Physik,* 19, 739 (1906).

[26] Dewar, *Proc. Roy. Soc. London,* **76A,** *325* (1906).

[27] Estreicher, *Bull. intern. acad. sci. Cracovie, 183* (1904).

[28] Shearer, *Phys. Rev.,* 17, 469 (1903).

[29] Lewis and Gibson, THIS JOURNAL, 39,2554 (1917).

contributions calculated by Lewis and Gibson of course make use of the corresponding temperatures determined by Eucken.

TABLE V

CALCULATION OF THE ENTROPY OF OXYGEN GAS

	This research, cal. per deg. per mole		Eucken, by Lewis and Gibson
0 to 11.75°K., extrapolation	0.321	Total 2.018	2.20
11.75 to 23.66°K., graphical	1.697		
Transition, 22.42/23.66	0.948		0.74
23.66 to 43.76°K., graphical	4.661		4.58
Transition, 177.6/43.76	4.058		3.94
43.76 to 54.39°K., graphical	2.397		2.62
Fusion, 106.3/54.39	1.954		1.95
54.39 to 90.13°K., graphical	6.462		6.52
Vaporization, 1628.8/90.13	18.07		17.72
Entropy of actual gas at boiling point	40.57 ± 0.1 E.U.		40.27

In order to make a comparison of this entropy value with that calculated from spectroscopic data, which is the primary purpose of this paper, it is necessary that the experimental value given above be corrected to the hypothetical perfect gas state. This may be done with the aid of Berthelot's equation and the thermodynamic equations involving the successive processes of expansion of the actual gas to zero pressure and of compression of perfect gas from zero pressure to one atmosphere. These lead to a net correction of $27T_c^3P/32T^3P_c$, as shown by Giauque and Wiebe.[3] With the aid of the critical data of Onnes, Dorsman and Holst,[30] namely, T, = 154.3°K. and P_c = 49.7 atmospheres, +0.17 entropy units is obtained as the value of this correction for oxygen gas at its boiling point. Hence the entropy of the hypothetical perfect oxygen gas at 90.13°K. is 40.74 E.U.

Entropy from Spectroscopic Data.—Dieke and Babcock[31] have obtained measurements of the fine structure of the atmospheric absorption bands of oxygen. Recently Mulliken[32] has given an interpretation which is satisfactory for the strong bands in this absorption and more recently Giauque and Johnston[33] have extended Mulliken's interpretation to include the weak A' band as well and so obtained a complete interpretation of the atmospheric bands. In the light of Mulliken's interpretation, the normal state of the molecule in oxygen gas is what is described by spectroscopists as a triplet *s* level. This means that the molecules in oxygen gas are differentiated into three forms of small energy difference characterized by the coupling between the angular momentum of electron spin

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[30] Onnes, Dorsman and Holst, *Comm. Phys. Lab. Univ. Leiden,* 145b (1914).

[31] Dieke and Babcock, *Proc. Nat. Acad. Sci., 13,* 670 (1927).

[32] Mulliken, Phys. *Rev.,* 32, 880 (1928).

[33] Giauque and Johnston, THIS JOURNAL, 51, 1436 (1929).

of the two unbalanced electrons in the oxygen molecule and the angular momentum of the rotating molecule. This coupling may be represented by drawing the momenta vectors oriented with respect to one another in parallel position, in anti-parallel position and in a position approximately at right angles. The molecules are further differentiated with respect to vibrational states with $n = {}^1/_2, {}^3/_2, {}^5/_2, \ldots\ldots$ The energy difference between the lowest state, the ${}^1/_2$ state, and the next higher state, the ${}^3/_2$ state, is sufficiently large (1554 wave numbers)[34] that at the boiling point of oxygen the number of molecules in the ${}^3/_2$ state is entirely negligible as shown by application of the Boltzmann factor. A still further differentiation of the oxygen molecules results from the quantized distribution of rotational energy among the various molecules. Characteristic of a homopolar molecule whose atoms have no nuclear spin, the alternately quantized rotation states are missing in oxygen, as in the diatomic helium molecule. This statement is supported by the quantum interpretation necessary to explain the Schumann bands of oxygen and by the interpretations of the atmospheric bands referred to above. The rotation states containing even-numbered units of angular momentum are missing and those present correspond to $j_k = 1, 3, 5, \ldots$ where j_k here is identical with the number of units of momentum possessed due to rotation of the molecule.

A further differentiation results due to the presence of isotopic molecules composed of an atom of oxygen of mass 16 combined with an atom of oxygen of mass 18 as shown by the interpretation[33] of the weak A' band. However, the very low intensities of the lines of the weak A' band when compared quantitatively with the intensities of the corresponding lines of the strong A band show that this isotope molecule is present in such a small amount as to have a negligible influence on the entropy.

The utilization of the energy levels of molecules, as obtained from spectroscopic data, in the calculation of entropy has been discussed by Giauque and Wiebe.[3] The equation

$$S_{\mathrm{E+R+V}} = R\left[\ln \Sigma_{e,n,m} p_{e,n,m} e^{-\epsilon_{e,n,m}/kT} + \frac{1}{kT}\,\frac{\Sigma_{e,n,m} p_{e,n,m}\epsilon_{e,n,m} e^{-\epsilon_{e,n,m}/kT}}{\Sigma_{e,n,m} p_{e,n,m} e^{-\epsilon_{e,n,m}/kT}}\right]$$

permits the calculation of the entropy due to all energy absorption other than that of translation. $\epsilon_{e,n,m}$ represents the energy of a certain state fixed with respect to the electronic configuration, the molecular vibration and molecular rotation; $p_{e,n,m}$ represents the corresponding *a priori* probability, or statistical weight of such a state, and $\Sigma_{e,n,m}$ indicates that terms within the summation sign are summed over all electronic, vibrational and rotational states of the molecule until it is apparent that further terms will add no appreciable contribution to the summation;

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[34] *Cf.* Birge, *Bull. Nat. Research* **Council, 11, 332 (1926).**

k represents the Boltzmann constant and e the base of the natural logarithms.

To the above entropy must be added the entropy due to the translation as given by the Sackur equation[35]

$$S_T = \frac{3}{2}R \ln M + \frac{3}{2}R \ln T + R \ln V + S_1$$

where R is the gas constant, T is the temperature on the absolute scale, M the molecular weight and V the molal volume in cc. $S_1 = 11.06$ cal. per degree per mole.

For the summations indicated above values were obtained from the data of Dieke and Babcock[31] for the energies corresponding to the first twenty-six rotation states in the normal oxygen molecule. Only odd-numbered values of j_k are present as explained previously. In keeping with the nomenclature of Mulliken,[32] F_1, F_2 and F_3 represent the three kinds of molecules resulting from differences in coupling between the angular momentum due to rotation of the molecule as a whole and the angular momentum due to spin of the electrons. F_1 represents the coupling with spin parallel to rotation, F_2 the coupling with spin approximately at right angles to the rotation vector and F_3 the coupling with spin antiparallel to rotation. j represents the total resultant angular momentum of the molecule and is given by the vector sum of j_k and s. Here s equals 1 and results from spin of the two unpaired electrons each electron contributing $^1/_2$ unit of angular momentum. The *a priori* probabilities necessary for use in the entropy equation given above are obtained from the values of j here listed by the relationship $p_{e,m,n} = 2j + 1$, as given by the wave mechanics. The energies for the molecules possessed of the F_2 coupling are derived by the use of the energy equation given by Dieke and Babcock,[31] with the constants derived from their P_1 and R_1 branches. The energies for molecules of corresponding j_k with F_1 or F_3 couplings were calculated from the F_2 energies by subtracting the approximate energy differences which exist between the F_2 and the F_1 or F_3 states. Several of these differences are tabulated by Mulliken and they have been smoothed out and extrapolated to higher j_k states by a graphical method.

TABLE VI

SUMS IN THE ENTROPY EQUATION FOR OXYGEN

$n = 1/2$, T = 90.13°K.

e	$\Sigma_{1/2,m} p_{1/2,m} e^{(-\epsilon_{1/2,m}/kT)}$	$(1/kT)\Sigma_{1/2,m} \epsilon_{1/2m} p_{1/2m} e^{(-\epsilon_{1/2,m}/kT)}$
F_1	28.574	24.635
F_2	21.686	21.748
F_3	17.333	18.990
$\Sigma_{e,1/2,m}$	67.593	65.373

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[35] (a) Sackur, Ann. *Physik*, 36, 598 (1911); (b) Tetrode, *ibid.*, **38,** 434 (1912); (c) Ehrenfest and Trkal, *Proc.* Acad. *Sci., Amsterdam,* 23, 162 (1920).

In Table VI we show the values obtained for the sums which appear in the entropy equation for T = 90.13°K. The sums are not affected within the numbers of decimals used by the inclusion of higher j_k states.

It is interesting to note that the oxygen molecules are quite unevenly distributed between the F_1, F_2 and F_3 states at the boiling point of oxygen gas. The distribution is 42.3% of F_1, 32.1% of F_2 and 25.6% of F_3. This uneven distribution is almost entirely due to the differences in the *a priori* probabilities. These differences are more pronounced for the low rotation states. The energies of the various states are nearly identical. We have calculated the contributions to these sums from the next higher vibration state and found them negligible for this temperature. Putting these sums into the entropy equation

$$S_{E+R+V} = 10.29 \text{ entropy units}$$

Combining this value with the 30.39 entropy units found for the contribution due to translation of the molecules as calculated with the Sackur[35a] equation for a monatomic gas, we find for the entropy of the hypothetical perfect oxygen gas at 1 atmosphere pressure and 90.13° K. the value 40.68 cal./deg. mole. The result of a similar calculation for a temperature of 298.1°K. is given in Table VII.

TABLE VII

SUMS IN THE ENTROPY EQUATION FOR OXYGEN

T = 298.1°K.

e	$\Sigma_{n,m} p_{n,m} e^{(-\epsilon_{n,m}/kT)}$	$1/kT\Sigma_{n,m} \epsilon_{n,m} p_{n,m} e^{(-\epsilon_{n,m}/kT)}$
n = 1/2, F_1	83.831	77.959
n = 1/2, F_2	72.882	72.628
n = 1/2, F_3	63.155	67.363
	219.868	217.950
n = 3/2, $\Sigma_{e,n,m}$	0.125	1.055
n = 5/2, $\Sigma_{e,n,m}$	.000	0.001
$\Sigma_{e,n,m}$	219.993	219.006

This leads to a value of $S_{298.1}$ = 49.03 E.U.

It will be of interest to compare the above method of calculating the rotational entropy with that proposed by Tetrode,[35b] who derived the equation $S_R = R \ln IT + S_2$ for the rotational entropy of a rigid molecule, where I is the moment of inertia in g.cm.^{2} and S_2 = 177.68. The above formula was derived for infinite temperature but for practical purposes holds quite well at ordinary temperatures. However, while this formula correctly represents the entropy of the molecular situation assumed by Tetrode, it fails to consider a number of factors which are now recognized as important in molecular behavior. Two of these are encountered in the case of the oxygen molecule. First, the triplet multiplicity of the various states of the oxygen molecule leads to an increase in the entropy of R ln 3 for the limiting case and by a slightly smaller amount at ordinary temperatures. Second, the homopolar character of the molecule combined with the non-spinning character of the oxygen nuclei results in the exclusion of alternate rotation states. This leads to a smaller entropy by R ln 2 for the limiting case. The net result of the above is that the rotational entropy of the oxygen molecule would be given approximately by

$$S_R = R \ln IT + R \ln \frac{3}{2} + S_2$$

The theoretical and experimental values are given in Table VIII. The "spectroscopic" values are those derived by the summation method.

TABLE VIII

COMPARISON OF SPECTROSCOPIC AND THIRD LAW VALUES OF THE ENTROPY OF OXYGEN

	T, °K.	90.13	298.1
	Spectroscopic, cal. per deg. per mole	40.68	49.03
Third law	Actual gas	40.57 ± 0.1	....
	Corrected to ideal state	40.7	49.1

The third law value given for 298.S°K. was obtained by adding the 0.17 E.U. correction for gas imperfection estimated by means of Berthelot's equation and the spectroscopic difference to the value obtained for the actual gas at the boiling point. The entropy was also calculated by utilizing the thermodynamic equation $\mathrm{d}P/\mathrm{d}T = \Delta S/\Delta V$ and vapor pressure measurements in place of the direct entropy of vaporization. The vapor pressure equation of Cath[13]

$$\log_{10} P(\text{atmos.}) = -\frac{419.31}{T} + 5.2365 - 0.00648T$$

was taken to represent the data. Later measurements[12] agree very closely with this equation. This was combined with Berthelot's equation, for which the constants have been given previously. For convenience the calculation was carried out at 71.40°K., where the vapor pressure of oxygen is 6.046 cm. and the molal volume of the liquid is 25.9 cc. from the work of Mattias and Onnes.[14]

The entropy of vaporization at this temperature and pressure was found to be 24.58 E.U., to which must be added a correction of 0.03 E.U. for gas imperfection of the Berthelot gas at this temperature and pressure. The entropy of the liquid at 71.40°K. was found to be 19.50 E.U. The entropy change accompanying the compression of ideal gas from 6.046 cm. to one atmosphere is −5.03 E.U. The increase in entropy on heating ideal gas from 71.40°K. to the boiling point at 90.13°K. is 1.62 E.U. when we assume a C_p of $^7/_2R$, which should be nearly correct. Then at 90.13°K., $S_{O_2} = 19.50 + 24.58 + 0.03 - 5.03 + 1.62 = 40.70$ E.U.

This value, which might be expected to contain a possible error of several tenths of an entropy unit, happens to be in excellent agreement with the theoretical value 40.68 E.U. and the more direct experimental value 40.74 E.U. This may be taken as a substantiation of the use of Berthelot's equation to represent gas imperfection.

Eucken, Karwat and Fried[36,37] have given the value $S_{298.1} = 49.04 \pm 0.2$ E.U. for oxygen.

This latter value is in excellent agreement with the theoretical value, although rather fortuitously so, as may be seen from the comparison made in Table V. In making the above calculation, Eucken, Karwat and Fried used the value 1629 obtained from an average of the available data rather than the value 1599 used by Lewis and Gibson in computing the entropy of vaporization given in Table V. Their selected value is identical with our experimental value.

It is well worth noting that the extended Tetrode equation leads to values which are practically identical with those calculated by the more reliable summation method. The value obtained at 90.13 is high by 0.02 E.U. while that at 298.1°K. is in exact agreement. While this close agreement is partially due to the fortuitous canceling of several effects it is to be expected that the Tetrode equation properly extended where necessary will usually give values correct to within a few hundredths of an entropy unit per mole at ordinary temperatures.

It is suggested that entropy values deduced from reliable spectroscopic data are preferable as a basis for thermodynamic calculations to the less accurate values obtained from heat capacity measurements and the third law. The values of the entropy obtained from spectroscopic data are for the ideal state of a gas, which is also the state of reference used in tabulating thermodynamic data.

The Paramagnetism of Solid Oxygen.—The magnetic susceptibility of solid oxygen has been investigated by Onnes and Perrier.[38] The susceptibility of the crystalline form stable below the boiling point of hydrogen has a very small positive temperature coefficient and appears to be approaching the absolute zero with a temperature coefficient of zero. From this some conclusions may be drawn as to the change in entropy with magnetic field strength. We have the thermodynamic equation[39]

$$\left(\frac{\partial S}{\partial \mathfrak{H}}\right)_{P,T} = \mathfrak{H}\left(\frac{\partial x}{\partial T}\right)_{P,\mathfrak{H}}$$

from which it is evident that a zero temperature coefficient of susceptibility corresponds to no change in entropy as the magnetic field strength is increased. While this in itself is not proof that the contribution to the

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[36] Eucken, Karwat and Fried, Z. *Physik,* 29, 1 (1924).

[37] "Thermodynamik und die freie Energie chemischer Substanzen," von Lewis und Randall, ubersetzt von Redlich, Julius Springer, Wien, 1927.

[38] Onnes and Perrier, *Comm. Phys. Lab. Univ. Leiden,* 116 (1910); 124A (1911); Perrier and Onnes, *ibid.,* 139C (1914).

[39] Giauque, THIS JOURNAL, 49, 1864 (1927).

entropy due to the magnetic system of the oxygen molecule is practically zero in this particular solid state, it is the condition imposed by the third law of thermodynamics for zero entropy in such systems. However, the agreement of the entropy calculated from our calorimetric measurements with that obtained from spectroscopic data shows that the magnetons in solid oxygen have little randomness at the temperatures of liquid hydrogen. It is therefore concluded that the magnetons have coupled with each other into what may be considered as a magneton crystal within the molecular crystal lattice of oxygen. The strong paramagnetism of solid oxygen must be regarded as due to what corresponds to a Paschen–Back effect in the solid—that is, a destruction of the coupling by the applied field as is observed in the case of some gaseous ions. This does not mean that the magneton crystal has been largely broken down by the fields of about 16,000 gauss which have been used for the susceptibility determinations, since the intensity of magnetization obtained is only 0.25% of the saturation value for two Bohr magnetons.

The small positive susceptibility obtained for many substances, and which has little temperature coefficient, may be due to the initial effect of the coupling breakdown which a sufficiently strong field could produce.

We wish to thank Mr. J. O. Clayton for assistance in making many of the measurements.

Summary

The heat capacities of the three crystalline forms of solid oxygen and of the liquid have been measured from 11.75°K. to the boiling point. The curves through the data are believed to represent the heat capacity of liquid oxygen to within 0.2 of 1%; of Solid I to within 0.3 of 1%; of Solid II to within 0.5 of 1%. For Solid III the inaccuracy of the curve may be somewhat larger, ranging from 1% at the upper extremity (23.66°K.) to possibly 5% at 12°K.

The transition temperatures were determined to be 23.66 ± 0.10°K. and 43.76 ± 0.05°K., respectively. The melting point was found to be 54.39 ± 0.05°K. and the boiling point 90.13 * 0.05°K.

Calorimetric measurements were made of the heats of transition, fusion and vaporization. Arranged in order of the transition at 23.66°, the transition at 43.76°, fusion and vaporization, these values are 22.42 ± 0.1, 177.6 * 0.5, 106.3 ± 0.3 and 1628.8 ± 1.6 calories per mole, respectively.

The entropy of oxygen gas at 90.13°K. and 1 atmosphere was calculated from the above data and the third law of thermodynamics, and found to be 40.57 ± 0.1 calories per degree per mole. Corrected to the ideal state with the aid of Berthelot's equation, a correction which amounted to +0.17 cal./degree/mole, this value was compared with that calculated by the accurate "summation" method from the molecular spectra of

oxygen gas. The two values are in almost exact agreement, showing that the triplet character of the oxygen molecule due to the unbalanced angular momentum of its two spinning electrons has contributed approximately R ln 3 to the entropy of gaseous oxygen, and also that the absence of alternate rotation levels in the oxygen molecule due to its homopolar nature results in an entropy of R ln 2 less than would be the case for a polar molecule of the same moment of inertia.

The entropy of oxygen gas at 298.1°K. was calculated by the "summation" method from the spectral data and found to be 49.03 calories per mole per degree. We believe that this is the best value for use in thermodynamic calculations.

It is also shown that the magnetons in the crystalline form of oxygen stable below 23.66°K. are not contributing appreciably to the entropy and must, therefore, be coupled in a non-random manner into what may be regarded as a magneton crystal within the ordinary molecular crystal lattice.

It is shown that the existing magnetic susceptibility data on solid oxygen are in agreement with the requirement of the third law of thermodynamics for zero entropy in magnetic systems, namely, that the temperature coefficient of the magnetic susceptibility should approach zero as the absolute zero of temperature is approached.

It is concluded that the large positive susceptibility of solid oxygen is due to the initial effect of a coupling breakdown induced by the applied field in analogy to the Paschen–Back effect in gaseous ions.

The general agreement of the various physical facts concerning the oxygen molecule in relation to the entropy and particularly the close agreement of the entropy as obtained by the two methods support our confidence that the third law of thermodynamics is an exact law.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXX. HALOGEN SUBSTITUTION PRODUCTS OF MONOGERMANE[1]

BY L. M. DENNIS AND P. R. JUDY

RECEIVED FEBRUARY 14, 1929 PUBLISHED AUGUST 7, 1929

Most of the possible halogen substitution products of methane and monosilane (SiH_4) of the types RHX_3, RH_2X_2 and RH_3X, have been prepared.[2] The purpose of the present investigation was the preparation and study of some of the analogous compounds of germanium.

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[1] This article is based upon part of the thesis presented to the Faculty of the Graduate School of Cornell University by P. R. Judy in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] See Landolt-Börnstein, "Physikalisch-chemiseheTabellen," 1923, Vol. I, p. 356.

Monochloromonogermane, GeH_3Cl, and Dichloromonogermane, GeH_2Cl_2.—These were prepared by the action of hydrogen chloride on monogermane in the presence of a catalyst.

Apparatus.—The apparatus was patterned after that of Laubengayer and Corey[3] and is shown in Fig. **1**. Stock's[4] modification of his mercury float valve was used. The bulb B_1, which is used as the reaction chamber, has a capacity of about **500** cc. and there is attached to the bottom of the bulb a tube 14 mm. wide and about **15** cm. long which is closed at the lower end. **A** tube **7** mm. in diameter and about 6 cm. long, open at its further end, is fused at right angles to the upper tube of the bulb at C. Just before beginning an experiment, a short tube of the same diameter, closed at one end and containing about **0.1** gram of anhydrous aluminum chloride, is fused to the open end of this side tube and the aluminum chloride is then sublimed into the bulb B_1, whereupon the side tube is sealed off at the point marked C. Three smaller bulbs, B_2, B_3 and B_4, attached to the line as shown, are used for the fractionation of the gases. K is a manometer for measuring gas pressures and E is a bulb for the weighing of separate samples. The space between the stopcocks S_2 and S_4, which would be full of air after D is detached and again attached to the chain, can be exhausted through the stopcock S_3. The volumes of various portions of the apparatus are calibrated by the use of the Hempel buret F in the manner described by Laubengayer and Corey. H is a calibrated tube which is used for measuring the volumes of liquids and determining their melting points. The bulbs B_5 and B_6 are storage bulbs of about one liter capacity which carry at the bottom short tubes and small bulbs for the application of the cooling baths.

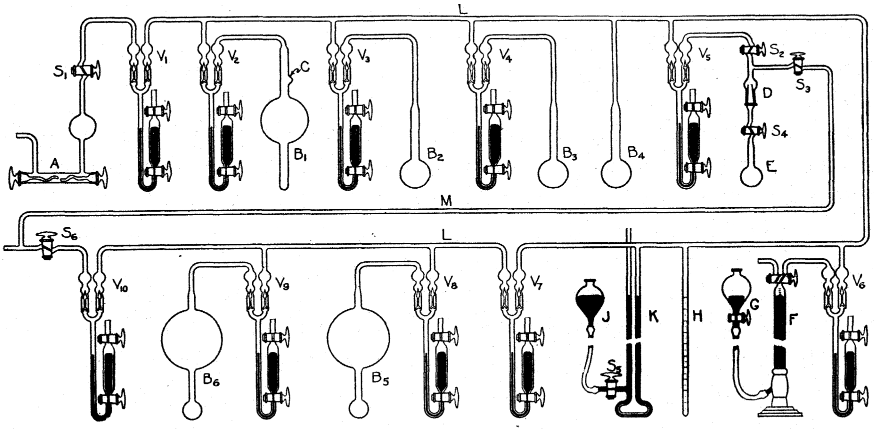

Fig. 1.

Before beginning an experiment the whole apparatus was freed from moisture by drawing through it air that had been purified by passage through soda lime, concentrated sulfuric acid and finally phosphorus pentoxide contained in the tube **A.**

Manipulation.—The monogermane that was used was a portion of the large sample of this gas that was prepared in **1923** for the study of the hydrides[5] of germanium, Determinations of the densities of two samples of this gas from different gas-holders gave

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[3] Laubengayer and Corey, J. Phys. *Chem.*, **30, 1043** (1925), Fig. **1.**

[4] Stock, *Z. Elektrochem.*, **23,** 33 **(1917).**

[5] Dennis, Corey and Moore, THIS JOURNAL, 46, **657 (1924).**

3.396 and 3 405, showing that the gas was quite pure and that it is very stable at room temperature over long periods of time. The gas was introduced through the stopcock S_6 into the bulbs B_5 and B_6.

Hydrogen chloride entirely free from air was introduced into the buret[3] F over mercury, where it could be measured.

The bulb B_1 was now evacuated, the catalyst was cautiously sublimed into it and the side tube was sealed by fusion at C. The change in the volume of the bulb which was thus caused was so small that recalibration of this part of the apparatus was unnecessary.

A known volume of monogermane, which was measured in the calibrated portion of the apparatus, was condensed in B_2 by means of liquid air. An amount of hydrogen chloride somewhat less than the theoretical volume required for the formation of monochloromonogermane was then drawn over into B_2 and condensed. The mixture of the two gases was then transferred to the reaction bulb, B_1, by cooling the tube attached to the bottom of the latter with liquid air and removing the refrigerant from around the bulb B_2. The valve V_2 was then closed.

Upon removing the liquid air from around the tube of B_1, the two liquids vaporized and reaction began at once. The application of heat was unnecessary. Equilibrium was reached in about thirty minutes.

After the reaction was complete, all gases other than hydrogen were frozen by liquid air and the hydrogen was measured.

In every experiment more hydrogen was evolved than corresponded to the formation of GeH_3Cl alone. Some dichloromonogermane was always simultaneously produced.

Fractionation.—After the hydrogen had been removed from the apparatus by the pump, the volatile residue in B_1 was transferred to B_2 to remove it from the catalyst. Unchanged monogermane (b. p. −90°) was distilled off at from −135 to −120° and condensed in B_4. Its volume was measured and it was then transferred to the storage bulbs. Hydrogen chloride (b. p. −83°) was then distilled off at from −120 to −90°, measured and removed.

The first slight rise in the manometer above −90° was at about −83°, at which temperature monochloromonogermane begins to come off. This was distilled over at −78°, and a quite pure product was usually obtained.

Dichloromonogermane began to come over at about −61° and distilled quite rapidly at −52°. Sharp separation of the two products was therefore possible on careful fractionation with the vacuum apparatus. The yield of the two compounds in the last experiment, after familiarity with the manipulation had been attained, was GeH_3Cl, 48%, and GeH_2Cl_2, 14%, of the GeH_4 that had reacted.

Analysis.—In the analysis of the corresponding compounds of silicon, Stock made use of the reaction with sodium hydroxide, in which hydrogen is quantitatively evolved. For example

$$SiH_3Cl + 3\ NaOH = Na_2SiO_3 + NaCl + 3\ H_2$$

This procedure was tried with the germanium compounds but when these were brought into contact with a solution of sodium hydroxide, germanium monoxide, not the dioxide, was formed, and the hydrogen set free was always considerably less than is called for in the equations

$$GeH_3Cl + H_2O = GeO + HCl + 2\ H_2$$
$$GeH_2Cl_2 + H_2O = GeO + 2\ HCl + H_2$$

Secondary reactions apparently take place, for even after prolonged treatment with sodium hydroxide, the odor of hydrides or chlorinated compounds of germanium could be detected.

The method of analysis that was finally adopted was to bring a known weight of the sample into the bulb E, close stopcock S_4, detach the bulb from D, cool E and then run into the bulb through the neck, first a dilute solution of potassium hydroxide, and then hydrogen peroxide. After decomposition of the sample and solution of the products were complete, the solution was acidified with nitric acid, the chlorine was precipitated by silver nitrate and after removal of the excess of silver from the filtrate, germanium was precipitated as the disulfide. The results of the analyses did not agree closely with the theoretical because of the unstable character of the compounds. They sufficed, however, to establish the identity of the monochloromonogermane and the dichloromonogermane and gave a ratio Ge:Cl of 1:1.03 in the first-named compound, and of 1:2.04 in the latter.

Properties of Dichloromonogermane and **Monochloromonogermane.**—Both substances are mobile, colorless liquids of peculiar, nauseating odor.

TABLE I

DICHLOROMONOGERMANE

Boiling point, 69.5°; melting point, −68'; density as liquid at −68°, 1.90; mol. wt., av. of four detns., 145.2; calcd., 145.54.

T, °C.	−54.7	−41.8	−31.5	−23.2	−11.5	−9.7	−3.5	0.4
P, mm.	1.3	2.1	5.9	9.3	19.3	21.6	30.6	36.9
T, °C.	2.5	8.4	13.8	20.7	26.4	31.3	35.8	40.2
P, mm.	41.1	58.1	72.2	110.0	142.1	176.3	214.2	258.2
T. °C.	44.3	48.5	53.5	58.0	61.6	65.3	68.7	71.2
P, mm.	304.9	358.8	431.2	511.7	588.2	660.6	739.4	802.3

The general equation derived from the above data is

$$\text{Log}_{10} P_{\text{mm.}} = -1742.7 \times \frac{1}{T} + 7.969$$

TABLE II

MONOCHLOROMONOGERMANE

Boiling point, 28°; melting point, −52°; density as liquid at −52°, 1.75; mol. wt., av. of seven detns., 110.92; calcd., 111.08.

T, °C.	−52	−44.2	−38.5	−32.8	−31.2	−24.6	−20.7
P, mm.	11.3	18.5	27.9	39.5	45.4	70.0	88.9
T, °C.	−14.8	− 9.4	− 5.0	2.1	5.5	8.8	
P, mm.	118.8	150.9	185.1	257.5	298.6	345.2	
T, °C.	11.9	16.3	20.7	24.6	27.6	29.5	
P, mm.	392.9	469.9	559.0	646.9	724.4	786.9	

The general equation derived from the above data is

$$\text{Log}_{10} P_{\text{mm.}} = -1527.4 \times \frac{1}{T} + 7.961$$

Both compounds fume when exposed to moist air, the walls of the container becoming coated with a film which is at first white and then becomes yellow, finally deepening to an orange tint. Considerable heat is liberated during this reaction. Water rapidly hydrolyzes the compounds and hydrogen is evolved. Absolute alcohol precipitates a white substance which dissolves to a yellow solution when an equal volume of water is added. Solutions of fixed alkali hydroxides precipitate an orange-colored compound, considerable hydrogen being set free. An alcoholic solution of potassium hydroxide yields a pale yellow precipitate, no hydrogen being evolved until water is added to the mixture.

Hydrogen chloride in the presence of aluminum chloride converts monochloromonogermane into dichloromonogermane with liberation of hydrogen. The dichloro compound does not further react with hydrogen chloride.

Ammonia acts instantly on both compounds, forming non-volatile, colored substances which decompose with explosive violence when heated in air.

Monochloromonogermane slowly breaks down at room temperature

$$2\ GeH_3Cl = GeH_4 + 2\ HCl + Ge$$

Dichloromonogermane decomposes much more rapidly. Among the products that are formed there were detected Ge, $GeCl_2$, GeH_4, HCl, GeH_3Cl, $GeCl_4$ and traces of hydrogen.

Monobromomonogermane, **GeH_3Br,** and Dibromomonogermane, **GeH_2Br_2.**—The method of preparation of these compounds was essentially the same as for the chlorine substitution products, hydrogen bromide replacing hydrogen chloride and aluminum bromide being used as the catalyst.

Reaction between the monogermane and the hydrogen bromide took place as soon as they were brought together, considerable heat being evolved. When reaction was complete, the bulb was surrounded by liquid air and the hydrogen was pumped off. The excess of monogermane was then removed at about —120". The separation of the bromination products by fractionation of the residue was difficult because of the instability of the compounds. This tendency to dissociate, even at quite low temperatures, rendered it impossible to obtain closely agreeing analytical results.

Properties of Dibromomonogermane and **Monobromomonogermane.**—Both compounds are colorless, mobile liquids of nauseating odor.

TABLE III

DIBROMOMONOGERMANE

Boiling point, 89°; melting point, −15°; density as liquid at 0°, 2.80

T, °C.	−26.6	− 5.6	0.6	5.9	15.5	21.7	27.4
P, mm.	1.2	3.7	6.5	9.6	15.7	28.3	36.1
T, °C.	34.1	35.2	38.9	43.2	49.5	57.2	
P, mm.	55.4	62.7	79.5	102.4	146.6	215.8	
T, °C.	63.9	69.2	75.3	79.2	81.1	82.3	
P, mm.	304.1	409.2	519.4	633.0	733.3	814.8	

The following general equation, derived from the above data, is accurate up to a temperature of 50°. At higher temperatures the pressure does not agree with the calculated values because of dissociation of the compound.

$$\text{Log}_{10} P_{\text{mm.}} = -2461.9 \times \frac{1}{T} + 9.798$$

TABLE IV

MONOBROMOMONOGERMANE

Boiling point, 52°; melting point, −32°; density as liquid at 29.5°, 2.34; mol. wt., 155.4; calcd., 155.54.

T, °C.	−44.6	−27.3	−16.4	−7.8	−3.3	4.8	10.9	15.4
***P*, mm.**	8.1	22.2	43.0	59.2	73.8	107.7	145.4	176.6
T, °C.	19.1	24.5	29.4	35.2	40.5	45.3	49.0	52.5
P, mm.	212.9	265.1	321.9	401.4	496.3	592.6	687.5	776.1

The general equation derived from the above data is:

$$\text{Log}_{10} P_{\text{mm.}} = -1614.7 \times \frac{1}{T} + 7.851$$

The chemical behavior of the monobromo- and dibromomonogermane is quite similar to that of the corresponding chlorine compounds.

Mono-iodomonogermane, CH_3I, and Di-iodomonogermane, CH_2I_2.—The iodine derivatives of methane are not very stable. Iodoform sublimes at 110° and begins to dissociate at this temperature. Tri-iodomonosilane boils at about 220° and begins to decompose at 150°. Tri-iodomonogermane was found to be unstable[6] above 0°. It was therefore to be expected that GeH_3I and GeH_2I_2 would, if their syntheses were successful, prove to be considerably less stable than the corresponding bromine and chlorine compounds of germanium.

In the preceding experiments it was found that monogermane reacts quietly upon hydrogen chloride in the presence of a catalyst with only slight rise of temperature, whereas with hydrogen bromide the reaction is vigorous and considerable heat is evolved. When equal volumes of monogermane and hydrogen iodide were mixed and were brought into a bulb containing aluminum bromide, the two gases reacted energetically and the bulb became quite hot near the reaction zone. A gas was evolved and drops of a colorless liquid formed on the catalyst. This liquid almost immediately turned yellow and soon changed to a solid. After three hours, the hydrogen that had been liberated was pumped off, and the unattacked monogermane was removed at −78°. Attempts to isolate GeH_3I and GeH_2I_2 by careful distillation in the vacuum apparatus were unsuccessful, and although evidence of the formation of those two compounds in the first stages of the reaction was obtained, it appeared that they then reacted with the hydrogen iodide to yield GeI_2 as the final product.

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[6] Brewer and Dennis, J. *Phys. Chem.*, 31, 1526 (1927).

$$\begin{aligned} GeH_3I + HI &= GeH_2I_2 + H_2 \\ GeH_2I_2 + HI &= GeHI_3 + H_2 \\ GeHI_3 &= GeI_2 + HI \end{aligned}$$

The formation of germanium di-iodide was established by first pumping off the hydrogen, monogermane and hydrogen iodide from the reaction bulb and then adding an excess of hydriodic acid to the yellow residue in the bulb. This dissolved the substance and the filtered solution deposited, on cooling, yellow, feathery crystals[6] of GeI_2. Some GeI_4 was also present, this being formed by the dissociation of some of the di-iodide

$$2\,GeI_2 = GeI_4 + Ge$$

The end-products of the reaction between monogermane and hydrogen iodide therefore appear to be germanium di-iodide, hydrogen and some germanium tetra-iodide.

Summary

This article deals with the preparation and properties of monochloromonogermane, dichloromonogermane, monobromomonogermane and dibromomonogermane. Evidence was obtained that indicated the formation of the corresponding iodo compounds which, however, could not be isolated because of their instability.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF PRINCETON UNIVERSITY]

POLARIZATION IN STANDARD CELLS

BY WENDELL S. NIEDERHAUSER AND GEORGE A. HULETT

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Introduction

Experimental studies of the effects of withdrawing current from standard cells[1] have shown these cells to be subject to a considerable degree of polarization, even at relatively low currents. It has also appeared that the polarization is roughly proportional to the strength of current, and that the cells recover quite satisfactorily following polarization, provided it has not been too prolonged. The passage of a current in the reverse direction through the cells also causes polarization, which, from the published results, appears to be somewhat more severe and of longer duration than that produced by discharging.[1e,f]

In all of the work mentioned above the cell has been considered as a

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[1] (a) Rayleigh and Sidgwick, *Trans. Roy. Soc. London,* **175A,** 411 (1884); (b) Threlfall and Pollock, *Phil. Mag.,* 28, 353 (1889); (c) Skinner, *ibid.,* **38,** 271 (1894); (d) Wulf, *Sitzb. Akad. Wiss. Wien,* Abt. IIa, 106, 562 (1897); (e) Barnett, *Phys. Rev.,* 18, 104 (1904); (f) Smith, *Trans. Roy. Soc. London,* **207A,** 393 (1908); (g) Wold, *Phys. Rev.,* 28, 132 (1909); (h) Hackett and Feely, *Sci. Proc. Roy. Dublin Soc.,* 15, 279 (1918).

single unit and the results refer to the total polarization. This is, of course, the sum of the polarizations of the individual electrodes, quantities which may be widely different. Jaeger, in a theoretical treatment of the polarization of such cells,[2] deals with the cases of the individual electrodes and mentions some experimental work done by Lindeck in which measurements were made of these separate effects. That a more complete report of Lindeck's work does not appear to have been published is regrettable, inasmuch as the results of the one experiment mentioned by Jaeger are in direct contradiction to those which are here presented. No other work on these single effects in standard cells has been found in the literature.

This paper presents the results of a study of the polarization of the individual limbs of the saturated, unsaturated and acid cadmium cells, and of the zinc cell at very low currents. Both the effects of discharging and of charging the cells are studied, and the results are interpreted in terms of the processes which take place at the separate electrodes during and after the passage of the current. No attempt is made to apply a theoretical treatment, such as that proposed by Jaeger, to the results, since the factors entering into such a treatment (ionic mobilities, rates of diffusion, and rates of solution and of crystallization of the salts present) are too uncertain to admit of accurate use.

General Experimental Methods

Preparation of Materials.—Mercury was purified by treatment with nitric acid followed by distillation under diminished air pressure.[3]

Cadmium amalgam (10%) was prepared by dissolving the weighed amount of Kahlbaum's purest, electrolytically prepared, stick cadmium in mercury on a steam-bath. Zinc amalgam (7%) was prepared in a similar manner.

Cadmium sulfate and zinc sulfate were recrystallized from solutions of the purest salts obtainable commercially.

The mercurous sulfate was prepared electrolytically in a 1.6 sulfuric acid solution (1.15 density), using a current density of 1 ampere per square decimeter of anode surface, according to the methods of Wolff[4] and Hulett.[5] The product varied from a fairly dark gray, finely divided material containing much mercury, to a pure white, somewhat coarser substance, according to the efficiency with which the anode surface of electrolyte was renewed by stirring during the preparation. The white material, the average grain size of which was about *25* microns, gave the most normal values when placed in cells and was used in most of the cells made in this work. A gray product having an average grain size of about 10 microns gave nearly identical cell values and was also employed in some of the work.

The saturated cadmium sulfate and zinc sulfate solutions were prepared by shaking an excess of the purified crystals with conductivity water in a thermostat at 25.0°. For unsaturated cells the electrolyte was prepared by dissolving the amount of the crystalline cadmium sulfate required to give a 43.06% solution (on the basis of the

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[2] Jaeger, *Ann. Physik,* [4] 14, 726 (1904).

[3] Hulett and Minchin, *Phys. **Rev.**,* 21, *388* (1905).

[4] Wolff, *Trans. Am. Electrochem. Soc.,* *5*, 49 (1904).

[5] Carhart and Hulett, *ibid.,* 5, 59 (1904).

anhydrous salt) in conductivity water in a stoppered bottle. Cells containing such a solution have a temperature coefficient of approximately zero.[6] The electrolyte for the acid cells was prepared by saturating a 0.1 *M* solution of sulfuric acid with cadmium sulfate.

In preparing the paste, the mercurous sulfate was filtered, with suction, in a Gooch crucible and washed several times with the electrolyte to be used in the cell. About one-third its volume of finely ground crystals (of zinc sulfate or cadmium sulfate as the case might be) was then added and the whole made up to a thin paste with the proper electrolyte.[7]

Cells.—The cells were the customary H-form, the internal diameter of the limbs being 10 mm. and that of the cross-arm somewhat less. Some special forms of cells used in the polarization studies will be described later. All cells were carefully cleaned and the platinum terminals amalgamated before filling. The materials were introduced by means of pipets, after which the cells were hermetically sealed. They were allowed to age for at least a month at constant temperature before use.

Constant-Temperature Bath.—The cells were kept in a constant-temperature bath as described in a previous paper by one of the present authors? A high grade mineral oil[9] was used as a bath liquid. The 25.00" point, at which the bath was maintained, was determined by means of a calibrated platinum resistance thermometer. Under the most favorable conditions the control of temperature could be maintained to ±0.002°.

Reference Standards.—Through the cooperation and kindness of the Bureau of Standards, a series of comparisons was run, during the course of this work, between the cells used as a basis of reference in this Laboratory and the Standards maintained by the Bureau in Washington. The Princeton reference group now consists of 15 cells, all of which are from fourteen to twenty-five years old, and have shown very constant values throughout their history. The mean value of the group has been established to an accuracy of I microvolt, on the present basis of the Bureau of Standards.

Measurement of E.m.f.—The electromotive force measurements reported in this work were made with a 5-dial Wolff potentiometer having a resistance of 15,000 ohms and a range from 0.00001 to 1.5 volts. The working current for the potentiometer was obtained from a two-cell standard battery[10] and was controlled by means of a manganin coil resistance box adjustable to 0.1 ohm. As a null instrument a high sensitivity moving coil galvanometer (Leeds and Northrup Co.) was used. The sensitivity of this instrument was such that, with the method of measurement described below, a deflection of 10 mm. or more (on the scale at a distance of one meter) was usually obtained for a change in potentiometer setting of 10 microvolts. This made the estimation of cell voltages to one microvolt relatively easy. For the elimination of parasitic electromotive forces in the circuit, reversing switches were placed in the working

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[6] Vosburgh and Eppley, THIS JOURNAL, 45, 2268 (1923).

[7] In this and subsequent operations, no attempt was made to prevent access of air to the materials, as suggested by (a) Vosburgh, THIS JOURNAL, 47, 1258 (1925); and (b) Eppley, *Trans. Am. Electrockem. Soc.*, **53**, 149 (1928). Evidence will be presented in a later paper [THIS JOURNAL, **51**, 2345 (1929)] to show that the high initial values of neutral cells, attributed by them to oxidation of the Hg_2SO_4 of the paste during its preparation, may be partially explained on another basis. Further experiments designed to test more directly the importance of Vosburgh's and Eppley's methods are being conducted in this Laboratory.

[8] Hulett, *Phys. Rev.*, **32**, 257 (1911).

[9] "Marcol" obtained from Stanco Distributors, Inc., New York City.

[10] Hulett, *Pkys. Rev.*, 27, 33 (1908).

battery circuit and the unknown e.m.f. circuit, so that these could be simultaneously reversed and, from the difference in galvanometer deflection obtained, a zero correction applied. The whole measuring outfit, including the baths in which the cells were kept, was carefully shielded against the effects of external e.m.f.'s.[11]

The method of measurement used was the differential method, employed at the Bureau of Standards.[12] Each cell to be measured was placed in opposition to a chosen cell whose e.m.f. had been previously established by a similar comparison with the cells of the reference group, and the difference in e.m.f. between these two cells determined. The potential of the unknown cell could then be calculated. Corrections for parasitic e.m.f.'s were made on every reading and with proper care final readings could be duplicated over and over without variation.

Measurement of Internal Resistances of Cells.—The measurement of the internal resistances of the cells, required in this work, presented some difficulty, as it was necessary that the method employed should not cause polarization. A modification of the capacity bridge method of Nernst and Haagn[13] was found most satisfactory. The introduction of a vacuum tube amplifier in the telephone circuit permitted an interchange of the microphone hummer, used as a source of audio frequency current, with the telephones, and the elimination of one condenser. Such a bridge is better balanced than the Nernst–Haagn arrangement. It was found to give a sharp sound minimum and was capable of adjustment well within the 0.5% accuracy required for our work.

To see whether such a measurement was injurious to a cell, potential measurements were made on several cells simultaneously with the resistance measurements. A change of about 10 microvolts could be detected while the resistance measurements were being made but this disappeared immediately upon the removal of the bridge connections. The resistances of most of the cells used were between 300 and **500** ohms.

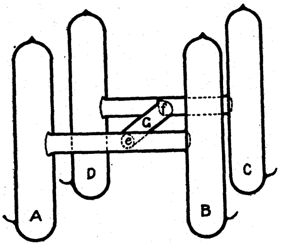

Fig. 1.—Four-legged cell used in polarization studies.

Methods of Study of the Polarization of the Separate Electrodes of Cells.—In order to determine how the polarization was distributed between the separate electrodes of the cell, a special form of cell vessel was devised (Fig. **1**). The mid-points of the cross-arms of two H-type cell vessels, AB and CD, were joined by a third cross-arm, ***G***. Limbs **A** and C were made cadmium amalgam-cadmium sulfate electrodes, while B and D were mercury–mercurous sulfate poles.

When a current was passed through one of the cell combinations thus made, say AB, the other electrodes, C and D, were entirely unaffected and could be used as reference electrodes to test the polarization of the working electrodes. Since **A** and C were of identical construction, the potential existing between them when the cell was on open circuit was very nearly, or exactly, zero. During the polarization of **A,** therefore, the potential difference measured from **A** to C (with a small zero correction if necessary) represented the total change in potential between the point e within the cell and the (external) terminal at A due to the passage of current. This total change in potential, ΔE_{Ta}, is the sum of two quantities, ΔE_{Ra}, which is the e.m.f. required to produce the flow of current through the resistance, R_a, between these two points, and ΔE_{Pa}, which is the polarization of the electrode.

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[11] White, THIS JOURNAL, **36, 2011 (1914).**

[12] Wolff and Waters, Bull. Bur. *Standards, 4,* **1 (1907).**

[13] Nernst and Haagn, *Z. **Elektrochem.***, 2, **493 *(1896).***

The current flowing through the cell may be obtained by measuring the potential difference, E_x, across a known resistance, R_x, in the external circuit. ΔE_{Ra} may then be calculated from Ohm's Law, and we obtain

$$\Delta E_{Pa} = \Delta E_{Ta} - \Delta E_{Ra} = \Delta E_{Ta} - \frac{E_x}{R_x} \times R_a$$

We may use the subscript, a, in the above equation to designate the amalgam limb of the cell. For the polarization of the mercury limb, ΔE_{Pm}, and of the cell as a whole, ΔE_{Pc}, similar relationships may be derived. The accuracy of the whole method was tested by comparing ΔE_{Pc} with the sum of ΔE_{Pa} and ΔE_{Pm}, each obtained from independent measurements. The agreement was exact at low currents, and never varied by more than 0.5% (due to leakage at the junction e) at the higher currents.

The determination of the resistances of the single limbs of the four-legged cells was accomplished by measuring the resistance across each of the six possible combinations of the four terminals of the cells (Fig. 1). The values thus obtained could be represented as sums of the resistances of the separate limbs of the cells (including in each case the resistance of the connecting cross-arm as far as the junctions e and f, respectively) and the cross-arm, G, connecting the two complete cells. The six equations representing these sums offered solutions for the resistances of the separate limbs. The results of different determinations agreed with each other to better than 0.5%. (There is a slight uncertainty at the junctions e and f, of course.)

In making the potential measurements called for in the above equations, the procedure was as follows. The e.m.f.'s of the two cells, AB and CD (Fig. 1), were first measured by the usual method. The potential differences between the amalgam limbs, A–C, and between the mercury limbs, B–D, were also measured. These latter were always zero or very small initially. The circuit connecting the cell AB across a high resistance[14] so as to discharge it, or in opposition to a larger e.m.f. (2 volts from a lead accumulator) with an appropriate high resistance in series, so as to charge the cell, was now closed. Experience having shown that the potential at the mercury limb was most affected by the passage of the current, special attention was paid to this quantity and readings of the change in it were taken as quickly as possible after closing the circuit and at frequent inter-

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[14] The high resistances required to secure the low currents used in this work were specially constructed by the International Resistor Company of Philadelphia, Pa. They consisted of a thin metallic coating on glass wires, insulated and mounted in sealed glass tubes. While these had appreciable temperature coefficients, and were not entirely unaffected by atmospheric conditions, they were much cheaper than coil resistances of the same denominations (0.1 to 10 megohms), and by placing them inside the thermostat they could be kept quite constant in value. Their values were checked from time to time to insure constancy, For all work below 100,000 ohms manganin coil resistances were used.

vals thereafter for at least one-half hour. Between these readings the change in potential at the amalgam limb and the total potentials of the polarized cell and of the unpolarized cell, CD, were also measured. A convenient arrangement of switches facilitated the change from one set of connections to another in making these readings. The unpolarized cell was, as expected, entirely unaffected by the passage of current through the other element. The recovery of the cell after opening the circuit was also observed. A second experiment was not started on a given cell until it had recovered from the effects of the last previous experiment. Inasmuch as the effect of charging was found to be more severe than the effect of discharging the cells, experiments on the polarization due to charging were never run on a given cell until all of the discharge measurements had been made.

A typical set of data from an experiment in which a cell was charged at the rate of 1.7 micro-amperes for thirty minutes is given below.

TYPICAL EXPERIMENTAL DATA

Cell U_3. $R_M = 193$ ohms. $R_A = 192$ ohms. $R_C = 385$ ohms. $R_X = 0.583 \times 10^6$ ohms.

Time, min.	B-D mmv.	A-C mmv.	CD volts	AB volts	E_x, volts[a]
0	− 12	0	1.018080	1.018068	.....
0.5	+650	...	......	......	.....
1.0	700	...	......	......	.....
2.0	764	...	......	......	.....
3.5	...	332	......	......	.....
5.0	862	...	......	......	.....
10.0	916	333	1.018080	......	.....
15.0	940	...	......	......	.....
16.5	...	...	......	1.019356	.....
22.0	...	...	......	......	1.00786
30.0	985	334	......	......	.....

[a] E_x changes as the polarization of AB changes. The percentage change in E_x is negligible, however, in the calculations for which it is used, and in its effect upon the magnitude of polarization of the cell.

From the above data, we calculated $\mathbf{I} = 1.729 \times 10^{-6}$ amperes; $\Delta E_{Rm} = 334$ mmv.; $\Delta E_{Ra} = 332$ mmv.; $\Delta E_{Rc} = 666$ mmv.

For the mercury electrode we obtain from the above data the following:

TABLE I

COURSE OF POLARIZATION OF MERCURY ELECTRODE WHILE CHARGING CELL U_3 AT A CURRENT OF 1.7 MICRO-AMPERES

Time, min.	0	0.5	1.0	2.0	5.0	10.0	15.0	30.0
ΔE_{Tm}, mmv.	0	662	712	776	874	928	952	997
ΔE_{Pm}, mmv.	0	328	378	442	540	594	618	663

For the amalgam electrode, on the other hand, $\Delta E_{Pa} = 0$ to 2 mmv. throughout the course of the experiment. The polarization is, therefore, practically entirely in the mercury limb.

The recovery observations (Table II) are given for the mercury limb only, as the recovery of the amalgam limb was practically immediate. Here, of course, the potential measurements represent polarization with no calculation other than a zero correction of 12 mmv.

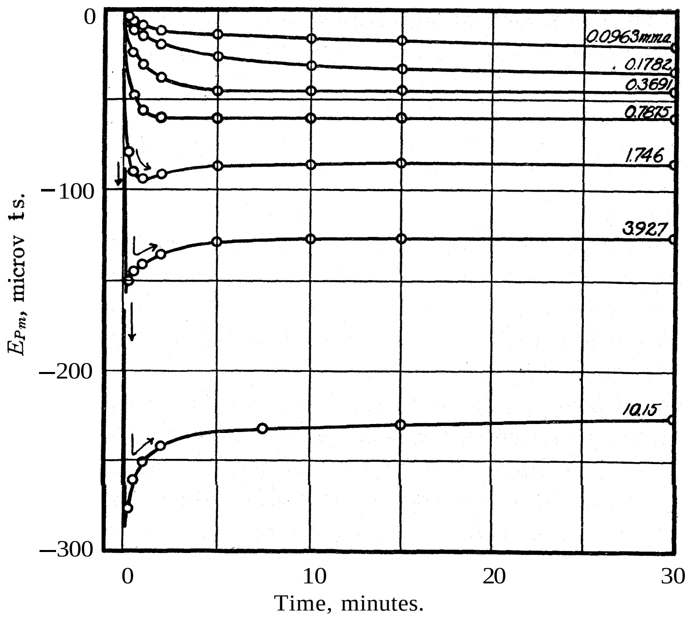
TABLE II

COURSE OF RECOVERY OP MERCURY ELECTRODE OR CELL U_3 AFTER THIRTY MINUTES' CHARGING AT 1.7 MICRO-AMPERES

Time, min.	0	1	2	5	10	15	30	60	120
R–D, mmv.	...	330	300	250	210	189	147	107	70
ΔE_{Pm}, mmv.	663[a]	342	312	262	222	201	159	119	82

[a] This value is obtained from Table I.

Observations on this cell were discontinued at the end of two hours. A week later the e.m.f. was still about 5 mmv. high.



Pig. 2.—Polarization in mercury limb at different discharging currents.

Results

Behavior of Mercury Limb during Discharge.—The course of polarization with time of discharge at the mercury electrode of a cell is shown for different currents in Fig. 2. The true polarizations, ΔE_{Pm}, of the electrode are plotted as ordinates with times as abscissas. The cell from which the data represented by these curves were obtained was a neutral unsaturated cadmium cell. The curves obtained for neutral saturated cadmium cells and zinc cells were entirely analogous to those here shown. The *magnitude* of the polarization at any given current differed from cell to cell, but the types of curves obtained as one increased the current were similar to those here shown throughout a number of studies of cells of each type.

It should be aoted that at low currents the polarization increases with time, but at a diminishing rate. Although cells were observed at currents of 0.1 micro-ampere for as long as fifty hours, they did not reach a steady state. It is to be assumed, however, that such a state would eventually be reached. As the rate of withdrawal of current is increased, the initial change in potential is more rapid, and a steady state is then reached in a very few minutes. A further increase in the current drawn produces a large initial polarization, followed by a period of apparent recovery, rapid at first and then more gradual. In some cases this recovery reached a maximum, after which the polarization again increased along a curve similar to that obtained at lower currents, while in other cases the recovery continued over a long period of time, apparently approaching a steady state.

Saturated cadmium cells made up with an acid electrolyte differed slightly in behavior from the cells above described. With a given sample of mercurous sulfate, acid cells required a current density nearly ten times as great as neutral cells to produce a polarization of given magnitude. They reached a steady state far more quickly than neutral cells. At 20 mma., for example, an acid cell became constant in e.m.f. in less than thirty seconds after the circuit was closed. The recovery effect, noted above, did not appear in an acid cell until a fifty-fold increase in current density was made.

Behavior of Mercury Limb **during** Charge.—The course of polarization at the mercury electrode of the same cell during charge is shown in Fig. **3.** The effect is, of course, opposite in direction to the effect of discharge. The slopes of the curves are greater at corresponding currents than for the discharge of the same cells, and a steady state is not reached as quickly as on discharge. The recovery tendency, noted in the discharge curves, is less pronounced, and soon gives way to the "normal" polarization effect. The results obtained on charging neutral saturated cadmium cells and zinc cells were strictly analogous to those obtained for the unsaturated cell as given in Fig. **3.** For the acid cells the differences in behavior from that of neutral cells noted in the experiments on discharging were found again to hold when the cells were charged.

Polarization over Longer Times.—A saturated cadmium cell was allowed to discharge for eleven days at a rate of 1.75 mma. Figure 4, Curve I, shows that the recovery tendency persisted throughout this time, and that the electrode recovered from an initial polarization of 2600 mmv. to within 300 mmv. of its value on open circuit. When the cirucit was then opened, the cell quickly recovered from the effects of polarization, and in less than nineteen hours the cathode had reached a value 20 mmv. higher than it had before the experiment was started. It maintained this value for three days, when the circuit was again closed, giving the curve shown as Curve II in the same figure. It will be noticed that the initial drop is now only 600 mmv., while the recovery seems to approach the same value as before. After sixty-five hours the circuit was opened. Recovery was complete (to the value 20 mmv. above the initial value of the cell) in ninety minutes and the circuit was then closed again. The initial drop was now only 300 mmv. and the curve quickly took up a continuation of Curve II. Eleven days of rest on open circuit followed, and, on again discharging at the same current, an initial polarization of 1400 mmv. was obtained. It is apparent that, although no change in the e.m.f. of the

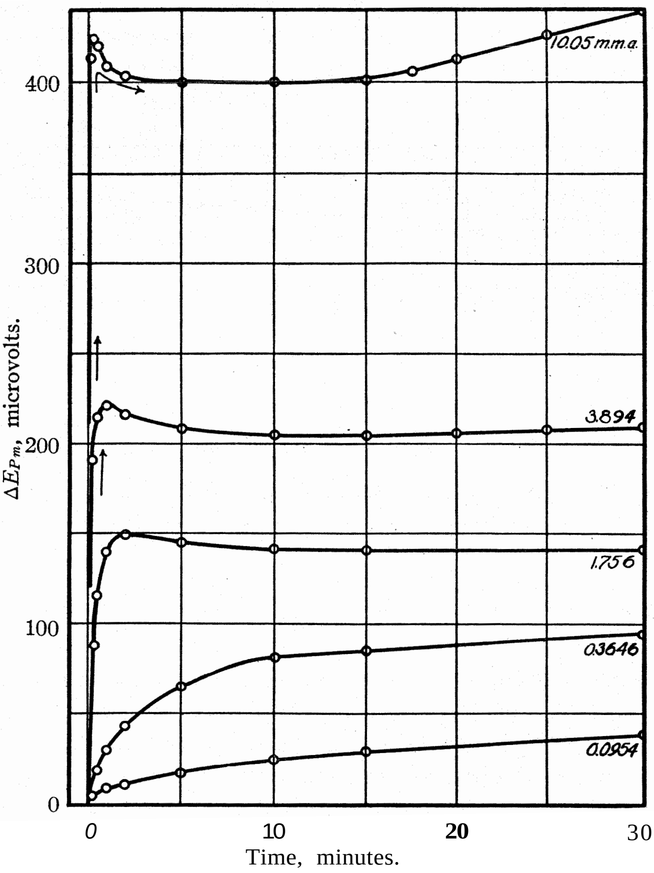


Fig. 3.—Polarization in mercury limb at different charging currents.

electrode took place during these periods of rest on open circuit, some process was going on which caused a decided increase in the *initial* polarization when the cell was later used to deliver current.

Inasmuch as the long time polarization of the cell had produced such a marked change in its behavior at the higher current, the question arose as to how its polarization at a much lower current would now compare with that previously observed for the cell. It was found that the polarization at a current of 0.1 micro-ampere was now 46 mmv., whereas it had formerly amounted to 168 mmv. at the same current.

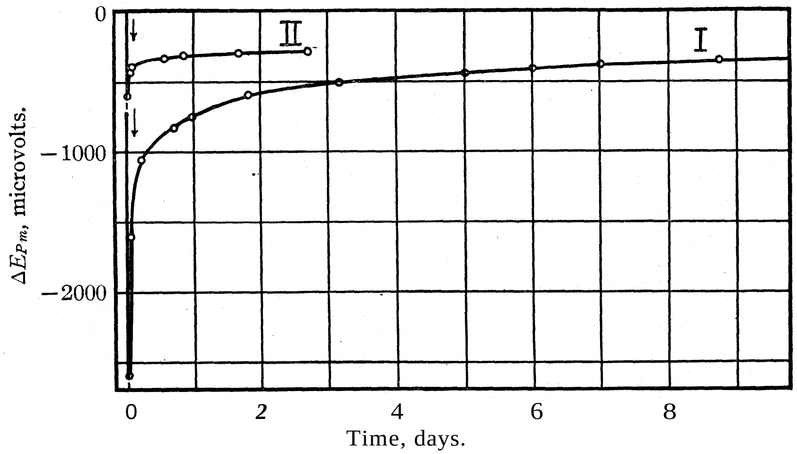


Fig. 4.—Effect of continued discharge at 1.75 micro-amperes upon mercury electrode.

The increase of 20 mmv. in the e.m.f. of the cell above described when allowed to rest after such a long time of polarization is interesting. Some old cells, particularly cells whose e.m.f. had shown a marked decrease, exhibited this effect, the increase in some cases being as great as 100 mmv. It usually disappeared within a few days after the circuit was opened.

Effect of Age of Cells upon their Polarization.—The discharge polarization of a cell was measured at a current of 10 micro-amperes six hours after it had been set up and placed in the bath. The recovery effect observed in older cells was also present in this cell, and its polarization was nearly as great at this time as it was found to be a month later, after the cell had been "aged" somewhat. Several cells built during the early spring of 1927, however, and tested with regard to their polarization in May and June of that year, were found to show an initial polarization nearly 30% higher at a given current when again measured ten months later. The characteristics of the polarization curve are the same, therefore, for new cells as for old ones, but the magnitude of polarization increases somewhat with the age of the cells.

Discharge of a Cell without Solid Depolarizer.—In order to see whether or not the presence of the solid mercurous sulfate had anything to do with the nature of the polarization curve, a cell was made in which the cathode limb contained a saturated solution of mercurous sulfate and cadmium sulfate with no solid salt. This cell was discharged at a rate of 10 mma. The recovery tendency was entirely absent. From an initial value of 313 mmv. the polarization increased in thirty minutes to 6003 mmv. When the circuit was opened the cell recovered to its initial value, though somewhat more slowly than *a* cell set up with the usual paste.

Internal Resistance of a Cell during Polarization.—The measurements of ΔE_{Tm}, from which the true polarization, ΔE_{Pm}, is obtained, include the ΔE_{Rm} term which is due to the internal resistance of the cell. A change in the internal resistance of the cell during the passage of current might, therefore, account for the recovery effect observed.[15]

To test this point the internal resistance of a cell was measured before and during polarization. The resistance during the passage of current was found to be the same, to within 0.1%, as it had been on open circuit. While these resistance measurements were being made, the polarization of the mercury limb of the cell decreased by an amount which, at the current drawn, would have necessitated a decrease in resistance greater than the total resistance of the cell if due to this cause. A change in the internal resistance of the cell is, therefore, excluded from any explanation of the recovery effect observed during the passage of current.

Recovery of the Mercury Electrode following Polarization.—The general nature of the recovery curve following the discharge of cells has been studied by other workers.[1] For the purpose of comparing the recovery following charge with that following discharge, however, results are here presented (Fig. 5) which show the recovery of the mercury electrode of a cell, (A) after sixty-five hours of discharge at 1.75 mma., and (B) after three and one-half hours' charge at 1.77 mma. The charge curve was the last obtained and the cell had rested for a month immediately beforehand. It is noted that three and one-half hours of charging produced a polarization six times as great as sixty-five hours of discharging at the same current. The recovery was, quite naturally, more rapid after discharge; but, although the effects of discharge disappeared one and one-half hours after the circuit was opened, the polarization following charge persisted for over two weeks. Similar observations were made on a large number of cells. Acid in the cells shortened the time required for recovery, both from discharge and from charge.

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[15] Changes in the resistance at the surfaces of the electrodes in certain electrolytic cells during the passage of current have been observed previously: (a) Burgess, *Trans. Am. Elertrochem. Soc., 7,* 51 *(1905);* (b) Holler, Bur. *Standards Sci. Papers, 20,* **153** *(1925).*

Polarization and Recovery of the Anodes of the Cells.—During the experiments on polarization of the mercury limb of the cell, observations were also made of the polarization of the amalgam limb. These observations showed, in general, that the polarization of the amalgam limb at a given current density was only 1/40 that of the mercury limb, and that the recovery tendency observed during polarization of the mercury limb was not present at these currents in the amalgam limb. The true polarization at these low currents was so small that it was, in many cases, of the same order as the uncertainty in determining ΔE_{Ra}.

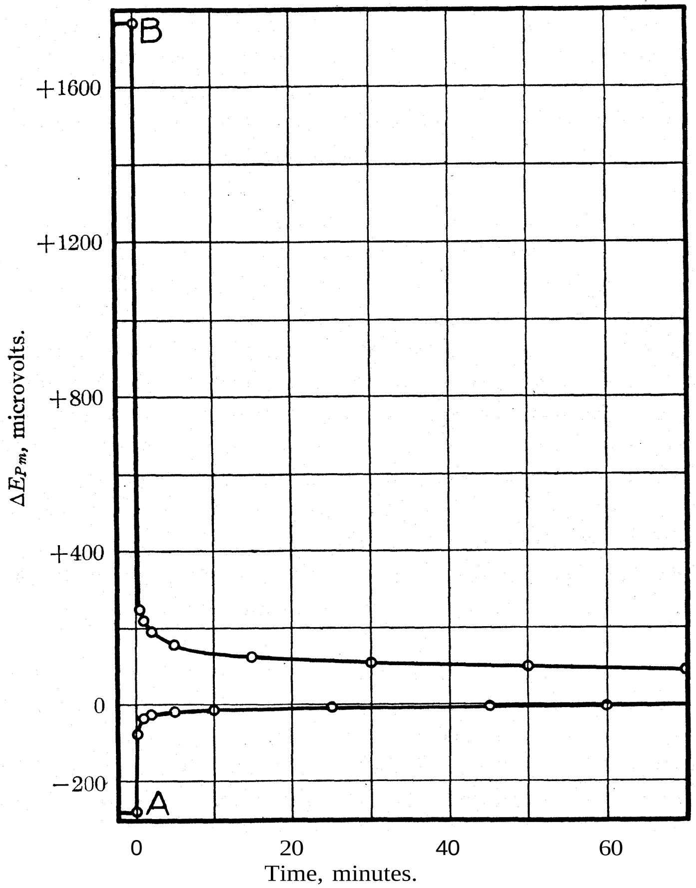

Fig. 5.—Recovery of mercury electrode from polarization: A, after 65 hours' discharging at 1.75 micro-amperes; B, after 35 hours' charging at 1.77 micro-amperes.

In order to compare the effects of charging and of discharging on the amalgam limb, therefore, a current of 15 mma. was passed through two amalgam limbs of a four-legged cell and the polarization and recovery of each limb (one of which had thus been charged and the other discharged) were observed by reference to the unpolarized mercury electrodes. The observations made during polarization are recorded in Table III.

TABLE III

COMPARISON OF EFFECTS OF CHARGE AND DISCHARGE ON AMALGAM LIMB OF A CELL

$I = 15$ micro-amperes

Time, minute.;		0	1	3	5	10	25	75	90
ΔE_{Ta}, mmv.	Discharge	0	−3838	−3841	−3844	−3848	−3856	−3874	−3879
	Charge	0	+4212	+4212	+4212	+4213	+4211	+4210	+4211

It is seen that the polarization of the amalgam electrode during charge is constant throughout at this current, while the polarization of the discharged electrode gradually increases. Calculation of ΔE_{Ra} gives for the discharged limb −3804 mmv. and for the charged limb +4216 mmv. with an uncertainty of 20 mmv. in each case. A calculation of ΔE_{Pa} is seen to be practically meaningless under these conditions.

During recovery on open circuit, however, the potential measurements give us the true polarization of the electrodes directly. The recovery of these limbs is shown in Table IV.

TABLE IV

RECOVERY OF AMALGAM LIMBS OR CELL FOLLOWING THE POLARIZATION SHOWN IN TABLE III

Time, minutes		0	1	5	15	30	75	4 hrs.	8 hrs.
ΔE_{Pa}, mmv.	After discharge	−75[a]	−42	−36	−30	−26	−19	−9	−2
	After charge	?	+2	0	0	0	0	0	0

[a] This value is obtained from Table III and is only approximate.

We observe from Tables III and IV that the polarization of the amalgam limb of the saturated cell is greater when it is being discharged than when it is being charged. Similar results were obtained from observations on the anodes of an unsaturated cadmium cell and of a zinc cell.

Discussion of Results

From the foregoing experiments it is seen that:

1. Neutral saturated and unsaturated cadmium cells and zinc cells are very similar in their behavior during the passage of current through them.
2. Most of the polarization in these cells is found in the mercury limbs.
3. At the mercury electrode the effect of charging is the more severe, while at the amalgam electrode discharging the cell causes the greater polarization.
4. A recovery effect, present only in the mercury limb of the cell, appears when the polarization occurs at the higher currents and tends to decrease the polarization of the cell.

5. This effect persists over long periods of time and produces marked changes in the subsequent behavior of the cell during polarization.

6. The magnitude of the initial polarization increases somewhat with the age of a cell.

7. Removal of the solid mercurous sulfate causes the disappearance of the recovery effect.

8. The presence of acid diminishes the magnitude of polarization and prevents the appearance of the recovery effect until greater currents are used than are required for its appearance in neutral cells.

9. No noticeable change in the resistance of a cell is found accompanying polarization.

10. The effects of polarization produced at the mercury electrode by discharging currents disappear more rapidly when the cell is left on open circuit than those of charging, while the converse is found to be the case at the amalgam electrode.

The neutral saturated cadmium cell will be used in the following discussion of the processes which occur during and following the passage of current through the cell. What is said of it may be applied equally well to the case of the zinc cell, and the additional considerations needed to explain the action of unsaturated and acid cadmium cells will be indicated.

In the mercury limb of the saturated cadmium cell we have a paste composed of crystals of mercurous sulfate and cadmium sulfate, and a saturated solution of these salts lying on a mercury surface. In the solution in contact with the mercury there are Cd^{++} ions, Hg_2^{++} ions, a few Hg^{++} ions, SO_4^{--} ions and the ions of water. When a current is passed through the cell so as to discharge it, positive ions from the solution are discharged into the mercury. We may expect that the ions discharged are principally the mercurous ions. Some cadmium ions are probably discharged, the metal going into solution in the mercury to form a very dilute amalgam. It is doubtful if hydrogen ions are discharged in any appreciable amount. The polarization of the electrode on discharge is due, then, to the removal of mercurous ions and cadmium ions from the solution immediately above the electrode and to the formation of an amalgam in the electrode. These are both concentration polarization effects.

In the solution the migration of positive ions toward the electrode tends to compensate for this type of polarization, as does the process of convection which sets in because of the diminished density of the solution immediately above the mercury surface. Also, cadmium sulfate and mercurous sulfate crystals in this region go into solution to make up the deficiency in concentration. At a given current a steady state would eventually be reached, at which the rate of depolarization due to the above processes would exactly equal the rate of polarization.

When a charging current is passed through the cell, mercury passes from the liquid metallic state into the ionic state in solution. This increases the concentration of mercurous ions in the solution, and results again in concentration polarization in the electrolyte. There is an additional complication in this case, however, because of the possibility of mercurous ions in the vicinity of the electrode being oxidized by the electrolytic action to the mercuric state. The accumulation of mercuric ions in such a neutral sulfate solution would result in the deposition of basic mercuric sulfate in the solid state.[16] There is no change in the composition of the mercury electrode during charging. The depolarizing processes here are those of electrolytic migration and of crystallization of both the mercurous sulfate and basic mercuric sulfate, and we would again expect a steady state to be reached between the polarizing and depolarizing actions.

When the circuit is opened, recovery begins. Diffusion, convection and solution or crystallization of the solid salts present act to restore saturation equilibrium in the electrolyte. Cadmium, which may have been deposited in the mercury during discharge, is removed by electrolytic displacement, and basic mercuric sulfate which was formed during charging redissolves, the mercuric ions being reduced by the mercury and deposited as mercurous sulfate.

The above discussion indicates that the electrolytic actions at the mercury electrode of the standard cell are not strictly reversible, and observed differences between the rates of polarization and recovery of this electrode when the cell is charged from those when it is discharged are easily understood from this point of view.

But this discussion does not indicate any explanation for the recovery effect observed during the polarization of a cell. The simple processes described above can only give a polarization curve which starts at a rapid rate and gradually slows down to a steady state that continues until one of the reacting substances is exhausted. No simple depolarizing process can explain the anomalous nature of the experimental curves, for such processes act only to reestablish a condition of equilibrium with the polarizing process. They cannot of themselves overbalance the polarizing action.

The recovery effect must be due to an independent change in the rate of one of the polarizing or depolarizing processes. A study of these various effects shows that the rates of most of them are dependent, either directly or indirectly, upon the strength of the current passing and, since this was practically constant, these rates could undergo no such change.

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[16] Smith, ref. 1f, observed the formation of this "green salt" during the charging of a cell, and Wolff, ref. 4, found "a basic salt containing mercuric compounds" formed when the electrolytic preparation of mercurous sulfate was attempted in a neutral solution of cadmium sulfate.

The rates of crystallization and of solution of the mercurous sulfate, however, while dependent upon the degree of unsaturation or supersaturation of the solution, and, therefore, indirectly upon the strength of current, are also a function of the state of the surface of the crystal. The fact that a cell from which the solid paste was omitted did not show the recovery effect lends support to the view that it is to this place we must look for an explanation.

If a crystal is well developed, as those of the paste must tend to become during long contact with their saturated solution, the removal or deposition of ions at its surface will take place more slowly than if the surface is irregular and imperfect. It is possible that at low currents the degree of unsaturation or of supersaturation of the solution in the vicinity of the mercurous sulfate crystals is such that solution or deposition takes place fairly uniformly over the whole crystal surface, without changing in any marked degree the nature of that surface. The polarization curve at such currents is perfectly normal. At higher currents, however, the degree of unsaturation or of supersaturation is much greater, and the solution or deposition of the ions at the crystal surfaces at the outset may produce a roughened surface which then has a greater rate of solution or crystallization than the original surface. The depolarizing power of such crystals is thus increased and the observed "recovery" takes place. This increase continues until a maximum is reached in the rate of interchange at the crystal surface and we may then have either a steady state in the polarization curve, or, if the other polarizing and depolarizing effects have not yet reached a state of equilibrium, the polarization may again increase until such a state is reached. When the cell is allowed to stand on open circuit, normal saturation equilibrium is first established, at which polarization disappears. The process of rebuilding the crystal face goes on, however, and as this progresses the magnitude of the initial polarization to be found on passing current through the cell is increased. The increase in the magnitude of polarization with the age of a cell would also be accounted for by this gradual building up of more perfect crystal surfaces.

Such changes in the rates of solution and crystallization of the mercurous sulfate do not explain the apparent increase in the equilibrium e.m.f. of the cells on open circuit after discharge. It is possible that this effect, which was observed principally in old cells that had fallen to low values, may be due to the removal, during polarization, of a thin film of basic mercurous sulfate which had been deposited on the crystals and prevented them from showing their normal solubility. Its removal gave the normal salt a chance to dissolve, and the value of the cell was temporarily increased after the circuit was opened. As the cell stood on open circuit, the coating of the basic salt was again formed and the value of the cell decreased.

No entirely satisfactory explanation has been found of the role of acid in decreasing the polarization of cells at a given current and preventing the appearance of the recovery effect at currents at which it appears in neutral cells. It seems that acid greatly accelerates the interchanges at the surface of the crystals, but just how such an effect operates is not clear.

That no difference was observed in the action of the mercury limbs of unsaturated cells from those of saturated cells indicates that the cadmium sulfate crystals mixed into the paste in order to maintain saturation of the solution in the one case do not play an important role in the polarization and depolarization of this limb.

In the amalgam limb of the cell we have a saturated solution of cadmium sulfate, with an excess of crystals, in contact with a two-phase cadmium amalgam. Cadmium ions go into solution from the amalgam during discharge and are deposited in metallic form in the amalgam during charge. The relative changes in cadmium-ion concentration in the electrolyte due to these actions are far smaller than the corresponding changes in mercurous-ion concentration at the other electrode, and it is natural, therefore, that the polarization at the amalgam electrode should be the less severe. Except for the possibility of some mercury from the amalgam passing into the ionic state during discharge, the electrolytic actions here appear to be perfectly reversible. The persistence of polarization following discharge, over the almost immediate recovery following charge, at this electrode, may be due to the presence of such ions in the solution, or to the fact that convection aids in the reestablishment of saturation equilibrium in the electrolyte in the latter case while in the former we are dependent upon diffusion alone.

Polarization during the Measurement of Cell Potentials.—In the measurement of cell potentials by the deflection method, currents as great as 10^{-8} amperes are occasionally drawn. The smallest current used in the polarization studies above described was 10^{-7} amperes, but a number of cells showed a polarization of 10 microvolts or more at this current. If the linear relationship between current and polarization holds at this current, it appears that some cells must be polarized to the extent of a microvolt or more during measurements that endeavor to determine their values to a single microvolt.

That such polarization does actually occur is indicated by the fact that the sensitivity of the galvanometer to a change of 10 microvolts in the potentiometer setting was always at least 10% lower when cells were being measured than that found when neutral resistances of the same magnitudes were substituted for them. In some cases this loss in galvanometer sensitivity was as great as 80% of its normal value. Such an extreme loss in galvanometer sensitivity is usually attributed to a high internal resistance in the cell. Calculation shows, however, that the resistance of such cells would have to be of the order of *2000* ohms, while their actual resistances were found by measurement to be less than 600 ohms in every case. There is no apparent reason for the high polarization shown by these cells. They were identical in construction, and in many cases had been made at the same time and of the same materials as cells that were less affected by the passage of current.

In actual practice the errors introduced by such polarization are very small and, to a certain extent, cancel one another in the course of a measurement. As a test of their effect a White potentiometer[17] having a range of 10,000 microvolts and adjustable to 1 microvolt was placed beside the Wolff instrument and alternate measurements of a number of cells were taken on the two instruments. In the case of the two cells which had been found to be most subject to polarization, the readings of the two instruments differed by 1 microvolt in the expected direction. In all other cases the agreement was exact. The use of an instrument of the White type is to be recommended, however, when measurements of high accuracy are undertaken.

Summary

The polarization of the separate electrodes of various types of standard cells under the influence of small charging and discharging currents has been studied experimentally, and the results interpreted in terms of the various polarizing and depolarizing actions which operate in the cells during and after a flow of current through them.

An interesting secondary effect of polarization has been found in the mercury limbs of cells, which causes an apparent recovery from polarization to take place during the passage of current. This recovery has been attributed to an increase in the rates of solution and of crystallization at the surfaces of the mercurous sulfate crystals.

It has been shown that cells are subject to polarization at the small currents that flow through them during measurements which undertake to estimate their potentials to microvolts by a deflection method. The actual error introduced because of such polarization is usually negligible.

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[17] (a) White, THIS JOURNAL, 36, 1868 (1914); (b) Leeds and Northrup Co , Bulletin No. 726, Philadelphia, Pa., 1927.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF PRINCETON UNIVERSITY]

HYSTERESIS IN STANDARD CELLS

BY WENDELL S. NIEDERHAUSER AND GEORGE A. HULETT

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Introduction

The theory has been advanced by Vosburgh[1] that the hysteresis observed when standard cells are subjected to a lowering of temperature is due to an excess of mercuric ions in the electrolyte. He considers that the equilibrium

$$Hg_2^{++} \rightleftharpoons Hg + Hg^{++}$$

which operates at the mercury surface in such cells is displaced to the right when the temperature of a cell is raised. The reverse reaction, which occurs on cooling, is a heterogeneous reaction and would be expected to take place more slowly than the dissociation caused by heating. Until the excess of mercuric ion thus present in a cell after cooling has been removed, the electromotive force is abnormally high.

On the basis of this theory he endeavored to account for earlier observations relating to hysteresis. The fact that cells containing *a* fine-grained sample of mercurous sulfate show less hysteresis than those containing a coarser material[2] he attributed to the smaller amount of solution in immediate contact with the mercury surface, and the reduced velocity of diffusion of mercuric ions to this surface in cells of the former type, making it possible for the mercury to maintain equilibrium with the solution at all times. The decrease in hysteresis caused by the presence of acid in a cell[2c,3] was considered to be due to a catalytic effect of the acid upon the above reaction. The increase in hysteresis with the age of a cell[3] could not be explained.

The temperature coefficient of the saturated cadmium cell is negative.[2b] A simple hysteresis on cooling the cell would be expected to appear as a low e.m.f., gradually rising toward the equilibrium value. The usual observation, however, is a rapid increase in e.m.f. to a value above that predicted by the temperature formula, followed by a slow decrease to equilibrium. The former type of hysteresis has been observed[4,2c] and associated with the use of large crystals of cadmium sulfate in the cells. It is obvious that we are dealing with two distinct effects and must turn to a

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[1] Vosburgh, THIS JOURNAL, 49, 78 (1927).

[2] (a) Von Steinwehr, *Z. Instrumentenk.*, **25**, 205 (1905); (b) Wolff, *Bull. Bur. Standards*, **5**, 309 (1908); (c) Vosburgh and Eppley, THIS JOURNAL, **46**, 104 (1924).

[3] *National Physical Lab. Reports, Electrician*, 71, 294 (1913).

[4] Wold, *Phys. Rev.*, 27, 329 (1908).

study of the sources of each of these effects if we would understand them more fully.[5]

This paper reports the results of an experimental study of the hysteresis shown by the separate electrodes of the cadmium cell. The results are not in agreement with Vosburgh's theory, and a more satisfactory explanation is presented for the observed facts.

Experimental Methods and Results

Apparatus and Materials.—The "adjustable cells"[6] used in studies of the cathode equilibrium in standard cells were a convenient form of cell for use in studying hysteresis in the separate limbs of cells. The anode and cathode half-cells of which these were made could be subjected separately to any desired temperature change, and tested under the new condition by measuring their potentials in opposition to another half-cell which had been brought to equilibrium previously at the new temperature.

The materials used in the construction of cells were those described in a previous paper.[7] The thermostats were maintained at 25 and 35°, respectively, with an accuracy of ±0.02°. E.m.f.'s were measured by the methods previously described,[7] with reference to standards maintained constantly at 25.00°. The effects of both heating and cooling the separate limbs of the cells were studied.

Hysteresis at the Anode.—Anode half-cells were transferred from the 25° bath to the 35° bath. A cathode half-cell which was kept in the 35° bath was used as a test electrode and the e.m.f.'s of the cells formed by combining this with the various anodes were measured at frequent intervals. In every case their values became constant within fifteen minutes after the change in temperature, and were in good agreement with the values calculated by use of the Wolff formula. After one hour the anodes were returned to the 25° bath and placed in opposition to cathodes which had been kept in this bath, and against which they had been tested previously. The results of measurements on two anodes, S_1, which contained large crystals of cadmium sulfate (average size about 2 mm.) and S_2, in which finely ground crystals were used, are given in Table I. The values are given as differences in microvolts from their former values at 25°.

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[5] F. E. Smith, *Phil. Mag.*, 19, 250 (1910), found an additional type of hysteresis that occurred in the amalgam when it was subjected to sudden temperature changes of 50° or more. He considered this to be due to a slow establishment of equilibrium between the liquid and solid phases of the amalgam. A more detailed theoretical investigation of this case, based upon the theory of solid solutions, was presented by S. W. J. Smith, *Phil. Mag.*, 20, 206 (1910). In the present work, which deals with manifestations of hysteresis likely to be met in the actual use of cells, we are not concerned with hysteresis of this type.

[6] Hulett, *Phys. Rev.*, 25, 16 (1907).

[7] Niederhauser and Hulett, THIS JOURNAL, 51, 2327 (1929).

TABLE I

HYSTERESIS IN ANODE LIMBS OF CELLS AFTER A SUDDEN CHANGE IN TEMPERATURE FROM 35 TO 25°

Time, minutes		10	15	20	25	30	35	40	50	65	85
Diff. from normal value at 25°, mmv.	S_1	−445	−345	−245	−195	−150	−115	−95	−57	−30	−14
	S_2	−2	0	0	0	0	0	0	0	0	0

The effect of large crystals of cadmium sulfate, first described by Wold, is shown by these results.

It was also found that placing a cell in the 35" bath for as short a time as three minutes caused hysteresis nearly as great as that shown above, when the cell was again cooled to 25°.

Hysteresis at the Cathode.—A similar method of study was applied to the cathode limbs of cells. Because of the practically complete absence of hysteresis in the anode limbs of cells containing finely-ground cadmium sulfate crystals, it was also possible to consider that hysteresis in such cells was located entirely in the cathodes. Some typical results are given in Table II, showing the hysteresis in the cathode limbs of cells containing a paste composed of different sized crystals of mercurous sulfate mixed with finely-powdered crystals of cadmium sulfate. The cells had been kept for one hour in the 35° bath and had attained constant values at that temperature, in practical agreement with the Wolff formula, well within that time. The average grain size of the mercurous sulfate used in the cells is indicated in each case.

TABLE II

HYSTERESIS IN CATHODE LIMBS OF CELLS AFTER A SUDDEN CHANGE IN TEMPERATURE FROM 35 TO 25°

Time, hours	Differences in mmv. from normal value at 25°			
	S_5 − 10μ	S_7 − 25μ	X_{53} − 50μ	X_{51} − 150μ[a]
1	+82	+90	+298	+936
5	63	77	197	842
10	55	70	169	774
24	44	58	117	655
48	38	47	79	482
72	35	41	68	333

[a] The large crystals used in cells X_{51} and X_{53} were obtained by recrystallization from a hot acid solution.

The relationship between the size of mercurous sulfate crystals and hysteresis in the cathode limb[2] is confirmed. It is also noted that the disappearance of hysteresis in this limb is very much slower than that in the anode limb.

Here again, placing the cells in the 35" bath for three minutes caused hysteresis, nearly as great as that shown above, when the cells were returned to 25°.

Effect of Temperature Changes on Cathodes Containing No Solid Mercurous Sulfate.—Cathode half-cells were constructed in which the electrolyte was a solution saturated with mercurous sulfate and cadmium sulfate at 25°, but which contained no solid mercurous sulfate."

The effect of temperature changes upon these elements was studied in the manner previously described. There was absolutely no hysteresis observed, either on heating or cooling. They reached constant values at 35° as quickly as temperature equilibrium was attained and showed a similar rapid return to their previous values at 25" when cooled to this temperature. The potential of the cell formed by this element and a normal anode half-cell at 35° was not that predicted for the normal cell by the Wolff formula. The formula predicts a decrease in potential of 563 mmv. on raising the temperature of the cell from 25 to 35°. This cell showed *a* decrease of 4120 mmv. Obviously the temperature coefficient of such a limb is very much different from one that contains solid salt.

Discussion

F. E. Smith[5] has shown that the temperature coefficient of the anode limb of the saturated cadmium cell is —0.00035 volt per degree, and that of the cathode limb is \$0.00031 volt per degree, making the over-all-temperature coefficient of the cell —0.00004 volt per degree, in agreement with the Wolff formula. The hysteresis shown in each limb of the cell corresponds then, to a slow continuous adjustment of that limb to equilibrium at the new temperature, and the anomalous nature of the hysteresis shown by the cell as a whole is due to the more rapid adjustment of the anode limb to the new temperature, leaving the cathode effect predominant.

In the anode limb the size of the cadmium sulfate crystals is found to determine the magnitude of hysteresis. The only function of these crystals is to maintain saturation in the solution. The solubility of cadmium sulfate increases with temperature, and a denser solution is formed at the surfaces of the crystals when the temperature is raised. Convection currents immediately carry this solution downward to the amalgam surface, where a layer of the saturated solution soon forms. Equilibrium at the electrode is thus quickly established. On cooling the cell, cadmium sulfate must crystallize from the solution and it can do this only at the surfaces of the crystals already present. It must reach these surfaces of the crystals already present. It must reach these surfaces by diffusion. In large-crystal cells the distances through which diffusion must take place are greater, and the available surface is less than in cells containing small crystals. The rate at which a state of supersaturation is relieved by crystallization of the excess solute is slower in the former case, and the

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[8] The solution was prepared by rotating a saturated solution of cadmium sulfate with solid mercurous sulfate and mercury (ref. 6). Solid cadmium sulfate was added to cells built with this solution so that saturation with respect to this salt would be maintained in the experiments which followed.

longer time required for such cells to reach equilibrium upon lowering the temperature is thus explained.

A similar explanation appears to be the most reasonable one to apply to the cathode limb. The abnormal temperature coefficient shown by a cathode that contained no solid mercurous sulfate indicates that an important role of this substance in the cell is to maintain saturation of the solution at the mercury surface at varying temperatures. The extremely long time taken for the disappearance of hysteresis in this limb in some cases is surprising. The high viscosity of the electrolyte is undoubtedly a factor in preventing a more rapid establishment of equilibrium.[9]

Vosburgh has entirely overlooked the change in solubility of mercurous sulfate with temperature in his consideration of hysteresis. The fact that cells containing no solid mercurous sulfate showed immediate responses to temperature changes is out of accord with this theory, which would predict a maximum of hysteresis in such cells.

The effect of acid in diminishing hysteresis is, from the point of view here presented, the same as its effect in diminishing polarization and accelerating the disappearance of polarization in cells.[7] It appears to increase the rates of crystallization and solution at the crystal surfaces.

The increase in magnitude of hysteresis with the age of cells, which Vosburgh was unable to explain, may be attributed to the same cause as the increase in polarization with the age of cells. We have considered that the surfaces of the crystals become more and more nearly perfect during long contact with their saturated solution. They then show a lower rate of solution or of crystallization than the imperfect crystals first placed in the cells. As the rate of crystallization is thus decreased with age, the hysteresis, which depends upon it, increases.

A study of the effect of temperature upon the solubility of mercurous sulfate in saturated cadmium sulfate solution, and of the mercurous–mercuric ion equilibrium in these solutions in contact with mercury, is now in progress. The results of this work will serve as a final test of the theories advanced to explain hysteresis in cells.

High Initial Values of Cells

Wolff[2b] observed that cells which showed abnormal hysteresis had also shown high initial values, which dropped rapidly during the first month after their construction and finally became nearly normal. He considered that this was because the cells were constructed in a laboratory where the temperature was different from that of the thermostats in which they were subsequently placed. But thermostats are usually maintained, except under

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[9] Menzies and Potter, THIS JOURNAL, 34, 1452 (1912), have shown that supersaturation may continue over very long periods of time in a viscous solution of H_3AsO_4, even though the solution is being stirred and a large number of nuclei are present to induce crystallization. The present case seems to be analogous to theirs.

special circumstances, at temperatures above room temperature, and we have seen that a change to higher temperatures is not attended by marked hysteresis. Wolff's explanation therefore, does not appear probable.

Vosburgh[10] considered that the high initial values were due to oxidation of the mercurous sulfate during the preparation of the paste and its introduction into the cells, the excess of mercuric salt being only slowly reduced at the mercury surface. He set up cells with great care to prevent access of air to the paste. The records of these cells, as well as those of cells set up without taking such precautions, are given in his papers. The cells made with protection from air are, on the whole, better than those made without such protection, yet some of the latter cells (Nos. 169 and 170) are quite as good as those of the protected group. The cells of the unprotected group which showed the most abnormal values were made from a different sample of mercurous sulfate than those of the protected group. It appears that there are factors other than the possible oxidation of the mercurous sulfate which must be considered in accounting for the high initial values of cells.

The fact noted in the hysteresis experiments that raising the temperature of a cell to 35° for as short a time as three minutes caused hysteresis effects when the cell was again returned to 25° suggested that a very short period of overheating during the construction of cells might cause them to show high initial values. As the temperature of the hand is usually above 30°, such overheating could come from simply holding the cells in the hand. Experimental evidence for this was obtained by warming old cells in the hand for several minutes and then returning them to the 25° bath from which they had been taken. In every case a large increase in e.m.f. was observed, which persisted for several weeks.

New cells were built, therefore, taking great care to avoid warming them above 25" at any time. The laboratory temperature was about 22° and the cells were cooled to 15° just before sealing. For the manipulations in the flame, during the sealing of these cells, they were held by means of a clamp fixed on the cross-arm, and an asbestos guard was used to protect the lower parts of the cells from the heat of the flame. No attempt was made to exclude oxygen from the cells, although the operations connected with the preparation and introduction of the paste were carried on as rapidly as possible.

Table III shows the values of cells made in this way compared with those of cells made by the old methods, in which the lower parts of the cells were supported in the fingers while sealing them. All of these cells were made from the same materials. The mercurous sulfate was a white electrolytic product, the average grain size of which was about 25 microns. Cells 55 and 56 were the first two cells set up in the new way, About a

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[10] **Vosburgh, THIS** JOURNAL, 47, 1225 (1925); 49, 78 (1927).

month later the next four cells, 57-60, were built. Of these four, 57 and 59 were sealed in the new way, while 58 and 60 received the same treatment throughout except for the sealing, which was done in the old way. The values of four other cells, 41-44, which were set up several months earlier and were not measured until they were a day old, are also included for comparison. The values of the cells of each group agreed with each other within a few microvolts, and are averaged in the table.

TABLE III

COMPARISON OF CELLS BUILT WITH AND WITHOUT CARE TO AVOID HEATING ABOVE 25° DURING CONSTRUCTION[a]

	E m f at 25 00°[b]			
Age of cells	55 and 56	57 and 59	58 and 60	41-44
15 minutes	1.018060	1.018036	1.018218	......
30 minutes	1.018068	1.018048	1.018206	......
75 minutes	1.018074	1.018058	1.018188	......
4 hours	1.018076	1.018071	1.018164	......
1 day	......	1.018072	1.018128	1.018121
2 days	1,018069	1.018070	1.018106	......
3 days	......	......	......	1.018099
5 days	......	1.018067	1.018089	......
1 week	1.018070	1.108070	1.018085	1.018084
2 weeks	1.018072	1 018074	1 018084	1.018080
1 month	0.018075	......	......	1.018080
2 months	......	......	......	1.018079

[a] Where blank spaces appear in the above table no readings were taken.

[b] The value of the Weston normal cell at this temperature, according to the Wolff formula, is 1.018074 volts.

The effect of such heating is clearly shown to account for the high initial values of these cells. It is interesting to note that cells made by the new method reached values within a few microvolts of the defined value in less than four hours, and, although they have varied slightly from time to time, they have been very close to that value ever since.

Summary

An experimental study has been made of the adjustment of the individual limbs of standard cells to temperature changes.

A new theory is suggested to explain hysteresis, which is based upon the rate of establishment of saturation equilibrium between the solution and the solid salts present in the cells.

The high values of new cells, which decrease during the first month or so, have been shown to be due, at least in part, to hysteresis which results from overheating them in the course of construction. A method of avoiding this trouble has given excellent results in the construction of cells which reached normal values within a few hours after they were built.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 46]

A STUDY OF THE SYSTEM SODIUM BICARBONATE–POTASSIUM BICARBONATE–WATER

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I. Introduction and Survey of Previous Work

Although studies have been made of the systems sodium bicarbonate–ammonium bicarbonate–water,[1] of sodium bicarbonate–sodium carbonate–water,[2] of potassium carbonate–sodium carbonate–water, including a very thorough investigation of the solid phases,[3] and of potassium bicarbonate–potassium carbonate–water,[4] no real investigation of the system sodium bicarbonate–potassium bicarbonate–water has been found in the literature.

The writer first became interested in this system during 1920, when it was suggested by Mr. W. D. Mount, Consulting Engineer of Lynchburg, Virginia, that he determine the practicability of developing commercially a process of obtaining soda ash as a by-product in the purification of potassium salts from Nebraska brines. A search of the literature at that time failed to disclose any study of the system sodium bicarbonate–potassium bicarbonate–water but the relative solubilities of sodium carbonate, potassium carbonate, sodium bicarbonate and potassium bicarbonate indicated that carbonating a saturated brine to convert the carbonates to bicarbonates, thereby precipitating the less soluble sodium bicarbonate, and then fractionally crystallizing the salts in solution, might offer a practical means of separating the salts commercially.

Dibbits has shown that solutions of sodium bicarbonate and of potassium bicarbonate lose appreciable quantities of carbon dioxide at even comparatively low temperatures, and that definite solubilities of the bicarbonates will only be found with definite partial pressures of carbon dioxide.[1,2,5] Since many investigators failed to consider loss of carbon dioxide from bicarbonate solutions, the solubility data given in the literature for pure $NaHCO_3$ and $KHCO_3$ are not always consistent. Of the references given, Fedotieff,[1] McCoy and Test,[2] Hill and Kill[4] and Dibbits[5] have taken into consideration the loss of carbon dioxide.

Since definite solubilities of the bicarbonates will be obtained only with

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[1] Fedotieff, *Z. physik. Chem.*, **49**, 162 (1904).

[2] McCoy and Test, THIS JOURNAL, 33, 476 (1911).

[3] Hill and Miller, ibid., 49, 669 (1927).

[4] Engel, *Ann. chim. phys.*, [6] **13**, 366–369 (1888); Hill and Hill, THIS JOURNAL, **49, 967** (1927).

[5] Dibbits, *J. prakt. Chem.*, [2] **10**, 417 (1874); Bodländer, Z. *physik.* Chem., **35, 32** (1900).

a definite partial pressure of carbon dioxide, and since practical application of the present study to the separation of sodium and potassium carbonates would be by passing a stream of carbon dioxide through the carbonates, it was decided to study the system $NaHCO_3$–$KHCO_3$–H_2O under the fixed condition that the partial pressure of carbon dioxide plus the partial pressure of water is equal to one atmosphere in the same way that Fedotieff[1] studied $NaHCO_3$–NH_4HCO_3–H_2O.

II. Theoretical Considerations

Since the restriction has been made that the partial pressure of carbon dioxide plus the partial pressure of water is equal to one atmosphere, carbon dioxide is not a component in the system. The components, therefore, can be considered as sodium bicarbonate, potassium bicarbonate and water. In the presence of one vapor and one liquid phase, three solid phases are required to make the system invariant. In the experimental work it has been found that at 20, 25 and 30° neither sodium bicarbonate nor potassium bicarbonate exists as a hydrate. Also, it has been found that at these temperatures solid solutions and double salts do not exist in equilibrium with solutions of any concentrations. Since only two solid phases have been found to separate from the solutions at these three temperatures, a quintuple point does not exist between the temperatures taken and the system cannot, therefore, become invariant between these temperatures. If the temperature is held constant, the system is fixed when the two phases sodium bicarbonate and potassium bicarbonate are present.

III. Apparatus and Procedure

The thermostat used was provided with a special shaker. The thermometer was graduated in tenths of a degree and was calibrated by the Bureau of Standards. Ordinary 300-cc. Erlenmeyer flasks were used to hold the solution and solids which were to be brought to equilibrium. These flasks were closed with two-holed rubber stoppers. A glass tube passed through one hole of the rubber stopper to well down into the solution in the flask, and when the flask was placed on the shaker in the thermostat, this glass tube was connected to a combination trap and carbon dioxide distributor by means of a light rubber tube. For the greater part of the run this glass dip-tube was raised above the solution. A second glass tube, about three inches in length, was placed in the second hole of the rubber stopper, flush with the bottom of the stopper and extending about two inches above the top of the stopper to prevent the possible entry of water from the thermostat. The combination trap and carbon dioxide distributor was connected to a cylinder of compressed carbon dioxide by means of a rubber tube.

In the earlier runs at 25° carbon dioxide was allowed to bubble through the solution for a considerable part of the run while the temperature was maintained at about 0.1" above the desired equilibrium temperature. It was later found that all the points determined with this procedure gave low solubility values, due to the temperature depression caused by bubbling carbon dioxide through the solution. It was also found, however, that unless carbon dioxide was bubbled through the solution for an appreciable time, considerable time would be required to convert the small amount of carbonate present to bicarbonate. The final procedure was to bubble carbon dioxide through the solutions for from two to four hours prior to starting the accurate temperature control, while holding the temperature 0.5 to 1° above the desired equilibrium temperature. In order to determine whether or not carbonates had been removed from the solutions, a small portion of the solution was, in some cases, removed from the flask and tested with phenolphthalein, which reacts approximately neutral to bicarbonate solution. The dip-tubes extending into the solution were then raised above the surface of the liquid, the carbon dioxide outlets on the Erlenmeyer flasks were capped and a slow stream of carbon dioxide was allowed to escape through a vent attached to the rubber tube leading to one of the Erlenmeyer flasks. By this method a pressure of carbon dioxide equal to the atmospheric pressure was maintained within the flasks, but carbon dioxide was not allowed to pass freely over the solution so as to cause a temperature depression. When the dip-tubes had been raised and the outlets capped, the temperature was adjusted to the equilibrium temperature and shaking continued to the first sampling period.

After the samples were taken, the air that had entered the Erlenmeyer flasks was displaced with carbon dioxide, the carbon dioxide outlets were again capped and carbon dioxide again was allowed to escape from the vent until the next sampling period.

For analysis of the solution and identification of the solid phases, the following determinations were in general made: (1) determination of the density of the solution at the equilibrium temperature by means of a pycnometer which had been standardized with distilled water at the equilibrium temperature; *(2)* determination of the total alkali in the solution by the titration of a 10-cc. sample with approximately normal hydrochloric acid, using methyl orange as an indicator; **(3)** determination of potassium present in the solution by means of the perchloric acid method; (4) determination of the total alkali bicarbonate in the solid phase which had been quickly washed and sucked fairly dry in a Buchner filter and then dried between folds of filter paper, or which had been whizzed until dry in a basket-type centrifuge; **(5)** determination of the ratio of sodium bicarbonate to potassium bicarbonate in the solid phase by heating the washed solid to a constant weight as carbonates and determining potassium by the perchloric acid method.

Due to the fact that the work had to be carried out in an atmosphere of carbon dioxide, an effort was made to shorten the runs as much as possible. Actually, much time was lost by trying to obtain consistent values after very short times (three or four hours) in the thermostat. Although the titration checks were fairly close (0.1 cc.) for an interval of about one hour, it was found that still better checks could be obtained. It would appear that the final rate at which equilibrium is obtained in the apparatus used is fairly slow, although equilibrium is approached very closely within a comparatively short time. Slight but consistent variations in the analyses established the greater certainty of the values obtained in longer runs. Equilibrium was considered to have been established when titrations separated by a two- or three-hour interval checked within 0.05 cc.

All pipets used in sampling were calibrated for delivery at each equilibrium temperature and the proper corrections for this delivery were made in the calculations.

IV. Materials

Merck's C. P. sodium bicarbonate was purified by dissolving in warm distilled water and recrystallizing with a stream of carbon dioxide passing through the solution.

The potassium bicarbonate employed was also a Merck product and was labeled "U. S. P. IX—Highest Purity—C. P." Before use it was dissolved in warm water and recrystallized with a stream of carbon dioxide passing through the solution.

V. Probable Errors in the Procedure

The temperature was maintained constant to 0.01" at 19.97°, to 0.03° at 25° and to 0.04° at 30.01". The maximum variation at 30° would affect the solubility of pure sodium bicarbonate, or of pure potassium bicarbonate, by about 1 part in 2000 and is therefore negligible.

In the analysis of the samples taken there was in no case a difference of over 0.1 cc. between check titrations. For most of the points at 19.97° and at 30.01°, the difference did not exceed 0.05 cc. In many cases the difference was not over 0.03 cc. Check potassium determinations did not differ more than 1 part in 350, except in one or two cases. Potassium checks of 1 in 1000 were not unusual and for most of the points variations not to exceed 1 part in 700 can be assumed.

The density determination was one of the most consistently reproducible determinations made. It is true that solutions of the bicarbonates tend to lose carbon dioxide, but the transfer to the pycnometer could be made quickly and the pycnometer sealed. The pycnometer was always brought to within 0.2" of the equilibrium temperature before being filled. The density determinations invariably checked in the third decimal place, while checks of 3 in the fourth decimal place were not unusual.

All of the above errors may, of course, be slightly increased by errors in taking the samples. Care was exercised, however, in keeping the pipets clean and in sampling, so that such errors were reduced to a minimum. It must be admitted that any difference method of analysis in which the combined errors may possibly all be thrown on that material present in the smallest percentage may result in comparatively large errors in the values found for the latter material. However, such a difference method of analysis is more accurate than the indirect determination of sodium and potassium bicarbonates by titrating, weighing as carbonates and solving a simultaneous equation for the quantities of sodium and potassium bicarbonates present. With the balance and compensation of errors that is obtained by plotting a curve from the data obtained, values read from the curve should be considerably more accurate than the maximum probable error for a single point.

At 25" the determinations of potassium by the perchloric acid method were made according to the procedure recommended by Scott,[6] with one exception. The procedure of Smith[7] was followed in all determinations at 19.97 and at 30.01°. In one case at 25° the two methods were run in

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[6] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1920.

[7] Smith, THIS JOURNAL, 47, 780 (1925).

parallel. A weight of 2.0771 g. of $KClO_4$ was obtained by the method of Scott and a weight of 2.0742 g. by the method of Smith. This is a variation of about 1 in 700, with the method of Smith giving a slightly lower value. In general, the procedure of Scott gave as good checks as the procedure of Smith, but the latter is decidedly smoother from the standpoint of manipulation and probably gives more accurate results, as claimed by Smith.

VI. Experimental Details and Tabulation of Results

A. Study of the System at a Temperature of 19.91 ± **0.01°.**—The work at approximately 20° was carried out after the procedure at 25° had been well developed and checked. For some reason solutions at 19.97°, fairly high in potassium, gave in two successive runs points which did not fit all of the curves, the deviations being comparatively large in some cases. The slowness with which equilibrium appeared to be reached suggested the possibility of solid solutions.

Analyses of the solid phases from runs which were continued considerably longer than usual established definitely that no solid solution or double salt existed along that portion of the curve where erratic results were obtained in the shorter runs. The longer runs with concentrations lying

TABLE I

DATA OBTAINED (EXCLUDING THE ERRATIC VALUES IN TWO RUNS)

No.	Density	G. per 100 g. of H_2O $NaHCO_3$	$KHCO_3$	G. per 100 g. of *soln.* $NaHCO_3$	$KHCO_3$	**Solid** phases
1	1.0625	9.55	0.00	8.72	0.00	$NaHCO_3$
2	1.0954	8.15	7.46	7.05	6.45	$NaHCO_3$
3	1.1309	7.03	15.60	5.73	12.72	$NaHCO_3$
4	1.1519	6.55	20.52	5.16	16.15	$NaHCO_3$[a]
5	1.1637	6.33	23.31	4.88	17.98	$NaHCO_3$[a]
6	1.1803	6.11	27.34	4.58	20.48	$NaHCO_3$[a]
7	1.1968	6.07	31.54	4.41	22.93	$NaHCO_3$–$KHCO_3$
8	1.1965	5.97	31.36	4.34	22.84	$NaHCO_3$–$KHCO_3$[b]
9	1.1897	3.85	32.05	2.84	23.58	$KHCO_3$
10	1.1830	1.86	32.74	1.38	24.32	$KHCO_3$
11	1.1777	0.00	33.30	0.00	24.98	$KHCO_3$[a]

[a] The solid phase was identified by analysis for all points except 11. Since hydrates of $KHCO_3$ had been found not to exist at Points 7, 8, 9 and 10, analysis of the solid at Point 11, other than *a* microscopic examination, was not considered necessary. Results of solid phase analyses are given for Points 4, 5 and 6, since it was in this area that solid solutions were suspected. A 0.6647-g. sample of solid from 4 that had been quickly washed and sucked fairly dry in a Buchner filter did not give a weighable quantity of $KClO_4$. Solid phases centrifuged but not washed from 5 and 6 gave the following analyses: 5, $NaHCO_3$, 99.25%; $KHCO_3$, 0.75%; 6, $NaHCO_3$, 98.99%; $KHCO_3$, 1.01 In the solid phase from both 5 and 6 a few minute crystals of $KHCO_3$ that formed during centrifuging could be identified with the microscope.

[b] With the aid of a reading glass and a small pair of tweezers a mechanical separation of the two solid phases was made. One analyzed 95.89% $KHCO_3$ and the other 94.80% $NaHCO_3$.

along the curve where erratic results had been previously obtained gave values which fitted closely into a smooth curve with the other points. No explanation can be offered for the comparative slowness with which equilibrium was reached.

B. Study of the System at a Temperature of 25 ± **0.03**°.—The work at *25"* was carried out first and it was during these runs that the technique was improved. While the values obtained at 25° are hardly, as a whole, as accurate as the values obtained on the 19.97" curves, and on the 30.01° curves, nevertheless, a very accurate check was made of the solubility of the pure sodium and potassium bicarbonates and of the solution composition at the break in the curve where both sodium and potassium bicarbonates are present as solid phases. Also, in plotting the values on the curve slightly greater weight was given to the later results.

TABLE 11

DATA OBTAINED AT 25 ± 0.03°

No.	Density	G. per 100 g of H_2O		G per 100 g of soln.		Solid phases
		$NaHCO_3$	$KHCO_3$	$NaHCO_3$	$KHCO_3$	
1	1.0648	10.31	0.00	9.34	0.00	$NaHCO_3$
2	1.0857	9.36	4.82	8 20	4.23	$NaHCO_3$
3	1.1035	8 72	8 98	7 41	7.63	$NaHCO_3$
4	1.1282	7.83	14.85	6.38	12.10	$NaHCO_3$
5	1.1547	7.21	21.12	5.62	16.46	$NaHCO_3$
6	1.1746	6 8 8	26.03	5.18	19.59	$NaHCO_3$
7	1.1732	6.81	25.69	5.14	19.39	$NaHCO_3$
8	1.1903	6.76	29.92	4.94	21.89	$NaHCO_3$
9	1 2087	6.58	34.59	4.66	24.50	$NaHCO_3$–$KHCO_3$[a]
10	1.2087	6.50	34.42	4.61	24.43	$NaHCO_3$–$KHCO_3$[b]
11	1.2042	5.24	34.95	3.74	24.93	$KHCO_3$
12	1.1998	3.77	35.08	2.72	25.27	$KHCO_3$
13	1.1977	3.32	35.48	2 39	25.56	$KHCO_3$
14	1.1927	1.55	35 93	1.12	26.13	$KHCO_3$
15	1.1884	0.00	36.57	0.00	2678	$KHCO_3$
16	1.1882	0.00	36 56	0.00	26.77	$KHCO_3$[a]
17	1.1879	0.00	36.58	0.00	26.78	$KHCO_3$[a]

[a] The solid phases were not analyzed in these runs, since they were all check runs and the solid phases were identified by the other runs at these same points. Runs 16 and 17 were made because it was realized that 15 did not check the values given in the literature to within the experimental errors.

[b] A rough mechanical separation of the two solid phases was made. One part analyzed 93.63% $NaHCO_3$ and 6.37% $KHCO_3$; the other, 95.86% $KHCO_3$ and 4.14% $NaHCO_3$.

C. Study of the System at a Temperature of **30.01** ± **0.04**°.—Due to the impossibility of keeping the room temperature within over 4 to 7° of the bath temperature, there was a tendency for crystals to separate out in the pipets. It was found advisable to warm the pipets slightly and then bring them to approximately the solution temperature by sucking up some of the solution, discarding it and then taking the sample. This same procedure was used in calibrating the pipets. This procedure in sampling is considered rapid and satisfactory.

All except two points on the curves were determined after the desirability of long runs was established, and from this standpoint the values for 30.01 ± 0.04° may be slightly superior to those on the 25° curves and some points on the 19.97° curves.

TABLE III

DATA OBTAINED

No.	Density	G. per 100 g. of H_2O $NaHCO_3$	G. per 100 g. of H_2O $KHCO_3$	G per 100 g. of soln. $NaHCO_3$	G per 100 g. of soln. $KHCO_3$	Solid phases
1	1.0673	11.05	0.00	9.95	0.00	$NaHCO_3$
2	1.0973	9.61	7.22	8.22	6.18	$NaHCO_3$
3	1.1196	8.90	12.39	7.34	10.22	$NaHCO_3$
4	1.1543	8.02	20.69	6.23	16.08	$NaHCO_3$
5	1.1887	7.48	29.26	5.47	21.40	$NaHCO_3$
6	1.2189	7.01	37.61	4.85	26.01	$NaHCO_3$–$KHCO_3$[a]
7	1.2189	6.97	37.64	4.82	26.03	$NaHCO_3$–$KHCO_3$[b]
8	1.2145	5.13	38.22	3.58	26.66	$KHCO_3$
9	1.2077	2.92	38.90	2.06	27.43	$KHCO_3$
10	1.1986	0.00	39.91	0.00	28.52	$KHCO_3$
11	1.1988	0.00	39.95	0.00	28.52	$KHCO_3$[a]
12	1.1990	0.00	39.92	0.00	28.53	$KHCO_3$[a]

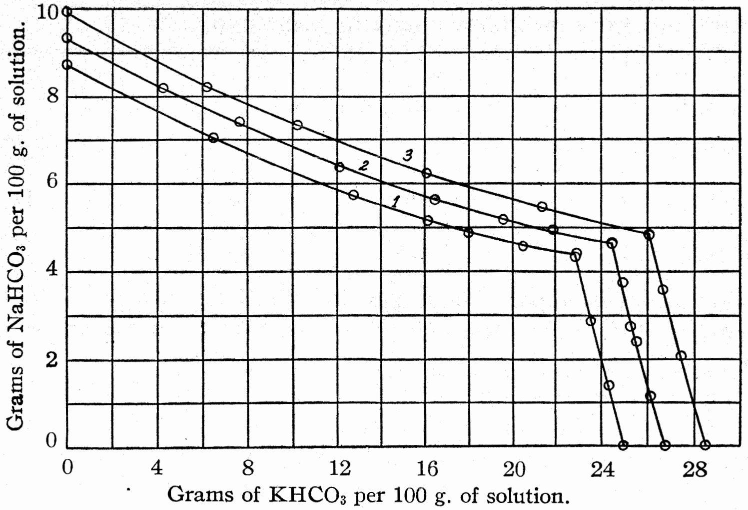
[a] Analysis of the solid phase was not made since these were check runs. Runs 11 and 12 were made after it was realized that the values found in 10 did not check to values found in the literature to within the experimental errors.

[b] A rough mechanical separation of the two solid phases was made. One gave an analysis of 91.74% $NaHCO_3$ and 8.26% $KHCO_3$. The other gave an analysis of 92.55% $KHCO_3$ and 7.45% $NaHCO_3$.

VII. Graphical Representation of Results

The triangular coordinate method of graphically representing results for ternary systems is particularly well adapted to those systems which show more than two solubility curves. Also, in general, lines drawn through the composition of the solution and the composition of the original complex can be made to give very definite indications of the composition of the solid phase.

In the present study an accurate knowledge of the exact composition of the original complex was somewhat difficult to obtain, (1) because the two salts used have a decided tendency to lose carbon dioxide and often contain appreciable quantities of carbonate, and (2) because bubbling carbon dioxide through the solution removed some water. In view of these facts, and the fact that there appeared to be only two solubility curves in the system at the temperatures chosen, it was felt that it would be more advisable to plot the weight of sodium bicarbonate against the weight of potassium bicarbonate while holding the weight of water or weight of solution constant. Curves constructed in this way can be plotted on a scale that makes them suitable for reading off interpolated values.

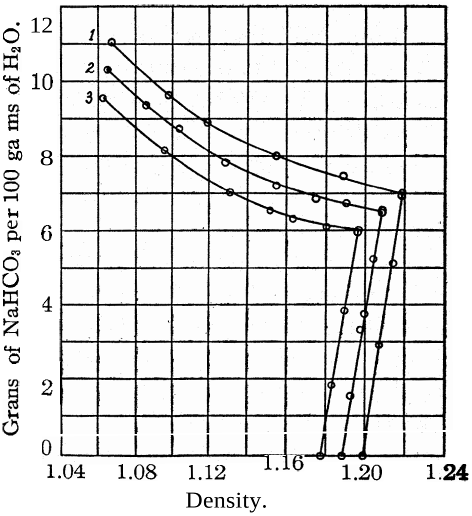


1, 19.97 ± 0.01°C.; 2, 25 ± 0.03°C.; 3, 30.01 ± 0.04°C.

Fig. 1.

Figures 1 and 2 are shown as illustrations of the curves plotted. Figure 1 shows the weight in grams of $NaHCO_3$ per 100 g. of solution plotted against the weight in grams of $KHCO_3$ per 100 g. of solution. Figure 2 shows the weight in grams of $NaHCO_3$ per 100 g. of water plotted against the density of the solution.

Various other smooth curves were plotted from the data obtained but are not considered worth reproducing as they can be readily made up from the tables. It may be of interest to note that when the grams of $KHCO_3$ per 100 g. of water are plotted against the density of the solution, points for the three temperatures all fall on approximately the same curve so long as $NaHCO_3$ is the solid phase.



1, 19.97 ± 0.01°C.; 2, 25 ± 0.03°C.; 3, 30.01 ± 0.04°C.

Fig. 2.

VIII. Comparison of Solubilities Found for Sodium Bicarbonate and Potassium Bicarbonate with Those Given in the Literature

The values found for the solubilities in water of pure sodium bicarbonate and pure potassium bicarbonate may be compared with values previously reported by other investigators, to whose work references have already been made.

TABLE IV

SODIUM BICARBONATP SOLUBILITY IN GRAMS PER 100 GRAMS OF WATER

	20°	25°	30"
Dibbits	9.6	10.35	11.1
Fedotieff	..	...	11.02
Tables I, II, III	9.55	10.31	11.05

McCoy and Test report 98.7 g. per liter for the solubility of sodium bicarbonate at 25°. The values given in Table II are equivalent to 99.4 g. per liter.

On the whole the values found check the better values given in the literature very closely. This is particularly true for values given by Fedotieff for 30°. Fedotieff did his work with the partial pressure of carbon dioxide plus the partial pressure of water vapor equal to the atmospheric pressure, and the values found in the two cases should check very closely.

TABLE V

POTASSIUM BICARBONATE—SOLUBILITY IN GRAMS PER 100 GRAMS OF WATER

	20°	25°	30°
Dibbits	33.2	36.1	39.0
Tables I, II, III	33.3	36.57	39.92

Hill and Hill find the solubility of potassium bicarbonate at 25° to be 26.55 g. per 100 g. of saturated solution, while the solubility given in Table II is 26.78 g. per 100 g. of saturated solution.

It is evident that the values found for the solubility of potassium bicarbonate are higher than the values given in the literature. However the results found, particularly those for 25 ± 0.03" and for 30.01 ± 0.04°, have been thoroughly checked and it has been found that they can be consistently duplicated with carefully calibrated volumetric apparatus, acid standardized at different times and chemicals crystallized separately from different packages. The values reported are consistently reproducible and, therefore, are offered as correct for the conditions under which the study was made.

A study of the work of Dibbits indicates that he made every effort to secure accuracy. Certain criticisms of his technique, however, may be made. Most important of these criticisms is the fact that he used a water-bath for temperature control and states, that, to avoid supersaturation, care was taken that the temperature should rise somewhat rather than drop. This procedure would certainly tend to give low results. According to Dibbits, loss of carbon dioxide at 30° might make a difference of about 0.3 in the values found. Such a difference would not account for the 0.92 variation between the value of Dibbits and that given in Table III. However, Dibbits' calculations of the extent to which loss of carbon dioxide might change the results probably did not represent equilibrium, and, therefore, may have indicated a smaller variation than would have been found at equilibrium.

The value obtained by Hill and Hill for the solubility of potassium bicarbonate at 25° is in good agreement with that of Dibbits, the value of Hill and Hill being equivalent to 36.15 g. per 100 g. of water. The value given in Table II, solubility of potassium bicarbonate in grams per 100 g. of solution, is 0.23 higher than the value of Hill and Hill. Such a variation is well outside of the experimental errors of the work recorded in this paper and, therefore, is significant. That the results found for sodium bicarbonate check the better values in the literature, while the results found for potassium bicarbonate are higher than the better values in the literature, is in agreement with the observation of Dibbits that the partial pressure of carbon dioxide is considerably higher over solutions of potassium bicarbonate than over solutions of sodium bicarbonate.

From the above comparison of results with the results of other investigators, it is indicated that the partial pressure of carbon dioxide over saturated solutions of potassium bicarbonate slightly exceeds the partial pressure of carbon dioxide maintained in the flasks during the experiments. Under such conditions, there would be present in the solutions a small amount of potassium carbonate. The carbonate content was not, however, sufficient to cause the solutions to react alkaline to phenolphthalein.

Even if the solubilities for potassium bicarbonate found in this study are higher than the results in the literature, because of the presence of a small amount of potassium carbonate, the results may be accepted as those that would be obtained when mixed solutions of the carbonates of sodium and potassium are treated at atmospheric pressure with a stream of carbon dioxide gas so as to convert the carbonates to bicarbonates and thereby effect a partial separation by precipitating one of the pure bicarbonates (usually sodium bicarbonate).

IX. Summary

1. The ternary system $NaHCO_3$–$KHCO_3$–H_2O has been studied at temperatures of 19.97 ± 0.01, 25 ± 0.03 and 30.01 ± 0.04° under the fixed condition that the sum of the partial pressures of carbon dioxide and of water vapor is equal to the atmospheric pressure.

2. The only solid phases that exist at these temperatures are $NaHCO_3$ and $KHCO_3$. The absence of hydrates, of solid solutions and of double salts at these temperatures has been definitely established.

3. The values found for the solubility of sodium bicarbonate check very closely the best values given in the literature.

4. The values found for the solubility of potassium bicarbonate, especially at 25 and at 30°, are higher than the best values found in the literature.

5. The composition of the solutions found in the ternary system, and the absence of complicating double salts and solid solutions, indicate that the present study might be of value in the commercial separation of sodium and potassium carbonates.

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[CONTRIBUTION FROM THE PHYSIKALISCHES INSTITUT, LEIPZIG, AND THE DEPARTMENT OF CHEMISTRY. DUKE UNIVERSITY]

THE DETERMINATION OF THE SOLUBILITY OF SLIGHTLY SOLUBLE LIQUIDS IN WATER AND THE SOLUBILITIES OF THE DICHLORO-ETHANES AND -PROPANES

BY PAUL GROSS

RECEIVED MARCH 9, 1929 PUBLISHED AUGUST 7, 1929

In order to make some measurements of the salting out effect of salts in water on the slightly soluble dichloro-ethanes and propanes, it became necessary to develop a method for determining their solubility in water and salt solutions. As this method is capable of considerable precision and as Hill[1] has pointed out that the methods for determining the solubility of liquids in liquids are in general very unsatisfactory, it is described here, together with the results of some solubility determinations made by its use.

The principle of the method is to prepare saturated solutions of the substance in water by shaking in a thermostat in the usual way. These solutions are then analyzed by the use of a liquid interferometer. The interferometer scale is calibrated by dissolving weighed amounts of the substance in weighed quantities of water.

Experimental

The instrument available was a Zeiss portable water interferometer with a glass comparison chamber **40** mm in length with two cells, in one of which a sample of the solution to be analyzed was placed and in the other the comparison or reference liquid. The general procedure and precautions to be observed in the use of the interferometer have been described in *a* number of places,[2] so it is unnecessary to repeat them here.

The scale readings on the compensator drum of the interferometer are not directly proportional to the number of interference bands it is necessary to shift to return the displaced upper bands to zero setting. The relation of bands shifted to scale divisions for different parts of the range of the instrument (which has a total of **3000** scale di-

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[1] Hill, THIS JOURNAL, 45, **1143 (1923).**

[2] See, for example, **L.** H. Adams, *ibid.*, 37, **1181 (1915).**

visions) was therefore found. From these, using the procedure described by Gans and Bose,[3] the following equation was obtained

$$S = R - 0.00003762\ R^2 \qquad (1)$$

where R is the observed scale reading and S is the reading which would be observed if the scale readings were directly proportional to the number of bands shifted.

Standard solutions of the substance being investigated were prepared by dissolving weighed amounts of it in 500 or 1000 g. of water. These were made by dropping a vial with a ground-in stopper containing the liquid into the weighed sample of water contained in a bottle with a well ground-in glass stopper. The stopper of the vial was loosened, the vial dropped in and its stopper after it. The bottle was then stoppered as quickly as possible. The weight of the water in the bottle was so chosen that the free space in the bottle after the vial and liquid were in was not more than 10 cc. in the case of the bottles holding 1000 cc.. and 5 cc. in the case of those holding 500 cc. By making this space small, appreciable loss of the liquid as vapor was thus avoided. These bottles were placed on a shaker and shaken until no more droplets of the liquid remained undissolved. This was quite easy to determine as these substances are heavier than water and have high refractive indices, so that even minute drops are readily visible. When solution was complete the scale reading R was found for a sample of the solution placed in the interferometer. Blank experiments made by shaking an empty vial in these bottles with 500 g. of water showed that no appreciable solution of the glass had taken place. The proper quantities of liquid to be used in making up the standard solutions can be found by a trial determination using about 0.2 g. of the substance per 1000 g. of water and from the value for the saturated solution made as described later.

From the observed readings R for these solutions the values of S were calculated by means of Equation 1. The values of S so obtained, when plotted, were found to be a linear function of the concentrations expressed as grams per 1000 g. of solution. This is illustrated by the data of Table I for 1,1-dichloro-ethane in water. The values of C are the concentrations in grams per 1000 g. of solution. The values of C' are those calculated from the equation

$$C' = 0.00507\ S \qquad (2)$$

where S is obtained as above.

TABLE I

DATA FOR 1,1-DICHLORO-ETHANE

S	C	C'	ΔC	% error
158	0.773	0.801	−0.028	3.5
345	1.711	1.750	− .039	2.2
475	2.443	2.408	+ .035	1.4
633	3.209	3.209	+ .000	0.0

Average error, 1.8%.

The direct proportionality of C and S was also established in another way, as follows. The saturated solutions of the substance were prepared by shaking 10–20 cc. of the liquid with about 500 g. of water in thin-walled cylindrical flasks in a large water thermostat regulated to 25 ± 0.01°.

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[3] Gans and Bose, *Z. Instrumentenkunde,* 36, 137 (1916).

Samples were withdrawn and analyzed at intervals of several hours until constant readings on the interferometer were obtained. About five hours was usually sufficient to effect equilibrium. However, the shaking in all cases was continued for at least twenty-four hours, and in most cases forty-eight hours elapsed before the final samples for the solubility values were taken. The readings for the saturated solutions were very reproducible. After equilibrium had been attained, one or more samples weighing several hundred grams were siphoned out of the shaking flask in the thermostat and run beneath the surface (to prevent loss by vaporization) of a weighed amount of water contained in a weighed flask with a ground-in stopper. The flask was then stoppered and weighed, and thus the weight of the saturated solution added was found. From this the dilution of this solution as a fraction of the saturated solution was calculated. The interferometer readings for these solutions were then determined. As an illustration of the accuracy with which the direct proportionality between readings and the concentrations figured as fractions of the saturated solution holds, some data for 1,1-dichloro-ethane are given in Table II.

TABLE II

DATA FOR 1,1-DICHLORO-ETHANE

Fraction of saturated solution	1.000	0.6901	0.4187
S, observed	993	685	414
S, calculated	...	685	416

From the data of Table II and Equation 2 the value of the solubility is calculated to be 5.035 g. per 1000 g. of solution and 5.06 g. per 1000 g. of water.

The substances used were purified from the best obtainable commercial samples by fractional distillation, using an all-glass still with a column 150 cm. long of the type previously described.[4] Temperatures were determined on thermometers standardized by the Bureau of Standards and pressures were read on a precision barometer.

1,1-Dichloro-ethane.—A fraction of 414 g. boiling between 57.0 and 57.1" was used. I. C. T. gives 57.3".

1,2-Dichloro-ethane.—A fraction containing 637 g. boiling from 83.6 to 83.8" was used. Timmermans[5] gives 83 69–83.71°.

1,2-Dichloropropane.—The commercial sample containing 1000 g. was fractionated three times and the constant-boiling fraction weighing 257 g. from the third fractionation was used. It boiled from 94.4 to 96.6". I. C. T. gives 96.8".

1,3-Dichloropropane.—A fraction of 507 g. boiling from 120.5 to 120.6' was used. Freund[6] gives a boiling point of 119.5° at 740 mm. This would correspond to a corrected boiling point of 120.3" if we assume that the value of *C* in Crafts' correction rule is $C = 0\,000100$, the same as the value given by Crafts for propylene bromide.

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[4] Gross and Wright, *J. Ind. Eng. Chem.*, **13,** 701 (1921).

[5] Timmermans, *Bull soc. chim. belg*, 24, *244* (1910).

[6] Freund, *Monatsh.*, 2, 639 (1881).

The value 125° given in I. C. T., Vol. I, p. 183, is evidently too high by at least 3°. It is apparently the value of Herzfelder[7] for a sample of 1,3-dichloropropane which, as Herzfelder himself states, contained iodine. The other values in the literature all agree in placing the boiling point at about 120 to 120.5°.

Carbon Tetrachloride.—This was a sample of Kahlbaum's "sulphur-free reagent for analytical use." It was used without further purification. The results for this substance are only preliminary.

The two remaining isomers of dichloropropane had originally been prepared and it was proposed also to measure their solubility. On trial it was found that they were hydrolyzed by water, as shown by the failure to ohtain constant saturation values. This was confirmed by testing for chlorides, which were shown to be present. In the case of each of the five substances used above, hydrolysis was carefully tested for and found absent.

The solubility data are given in Table III. The estimated errors of these solubility values are as follows: for 1,2-dichloro-ethane, 1%; for 1,1-dichloro-ethane, 2.0%; for the dichloropropanes, 2.5%. The error for the carbon tetrachloride is about 5%, as in this case the limit of the sensitivity of the interferometer with the 40-mm. chamber available was approached. This value must therefore be regarded as only preliminary. It is planned to repeat the measurements for this substance with a purer sample and with a longer (80-mm.) liquid chamber.

The sensitivity of the method can be appreciated when it is realized that an error of 2.0% in the solubility value of 1,1-dichloro-ethane represents an error of 0.01% on the total composition of the solution.

TABLE III

SOLUBILITY DATA

	Solubility in water at 25°, g. per 100 g. of H_2O	Moles per 1000 g. of H_2O
1,1-Dichloro-ethane	0.506	0.0511
1,2-Dichloro-ethane	.865	.0874
1,2-Dichloropropane	.280	.0248
1,3-Dichloropropane	.273	.0243
Carbon tetrachloride	.077	.0050

Rex[8] gives values for the solubility of three of these substances in water at 20 and 30°. From these the following values for the solubility in grams per 100 g. of water at 25° were interpolated: for 1,1-dichloro-ethane, 0.545; for 1,2-dichloro-ethane, 0.881; for carbon tetrachloride, 0.082. These values are consistently higher than those given above but this seems probable in view of the method used by Rex, which was to measure in a capillary the volume of liquid before and after saturating a known amount of water with it and determining the solubility from the difference in volume. Apparently no allowance was made for possible loss of the liquid which may have adhered to the walls of the larger vessel, containing the water,

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[7] Herzfelder, *Ber.*, 26, 2434 (1893).

[8] Rex, *Z. physik. Chem.*, 55, 365 (1906).

to which the capillary was sealed. This loss would result in a larger apparent solubility.

The method as outlined has also been used to determine the solubility of these substances in salt solutions, in particular in 0.5 *M* potassium chloride and 0.5 *M* magnesium sulfate. The procedure is in all particulars the same as for water. A large volume of the salt solution of the desired concentration is made up and used throughout for dilutions, standard solutions, comparison solutions in the interferometer, etc., in the place of distilled water. In general, there appears to be no reason why the method should not be applicable to solubility measurements in practically any colorless aqueous solutions for any type of substance. Measurements of solubilities in non-aqueous solvents are also possible but these would in many cases involve difficulties inherent in the construction of the interferometer itself, which is primarily designed for aqueous solutions.[9]

In conclusion I take this opportunity to thank Professor Peter Debye for placing facilities at my disposal at the Physikalisches Institut, Leipzig, with which part of the work was done, and for valuable suggestions and advice.

Summary

1. A method for the determination of the solubility of difficultly soluble liquids in water and aqueous solutions is described.

2. The solubilities of 1,1-dichloro-ethane, 1,2-dichloro-ethane, 1,2-dichloropropane and 1,3-dichloropropane are given. A preliminary value for the solubility of carbon tetrachloride is also given.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 205]

THE ACTIVATION OF OXYGEN BY ELECTRON IMPACT

BY ROBERT H. DALTON

RECEIVED MARCH 11, 1929 PUBLISHED AUGUST 7, 1929

Introduction

The purpose of this research was to study the chemical behavior of oxygen activated by electron impact and to measure the energy necessary for its activation. The general plan was to use an apparatus similar to that employed by Glockler, Baxter and Dalton[1] in the study of the reaction between copper oxide and active hydrogen.

The oxygen was introduced at pressures of 0.05–0.4 mm. of mercury into a four-electrode tube connected with a liquid-air trap and a Pirani pressure gage. A four-electrode tube was used in order that the energy loss of the

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[9] In this connection see Cohen and Bruins, Proc. Acad. *Sci. Amsterdam,* 24, 114 (1921).

[1] Glockler, Baxter and Dalton, THIS JOURNAL, 49, 58 (1927).

electrons might be studied by making current-potential curves as done by Franck[2] and others. With this arrangement it was possible to follow the course of any reaction which involved a change in the number of molecules or produced a substance condensable in liquid air. It was, of course, not possible to use gases which would undergo reaction when exposed to the hot filament. Several reactions were tried; the one finally studied was that of the activated oxygen with solid carbon to form carbon dioxide.

Materials and Apparatus.--The oxygen was obtained by heating mercuric oxide which was contained in a bulb attached to the apparatus. The mercuric oxide had been previously prepared in the apparatus by boiling mercury for some time with well-dried tank oxygen.

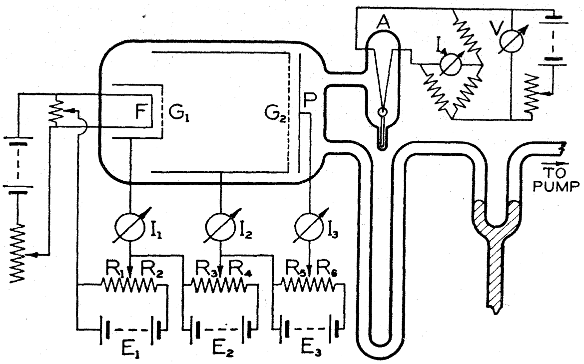

Fig. 1.

The carbon was present in the form of lampblack deposited on the end of grid G_2 with a smoky gas–oxygen flame, except in the case of a preliminary experiment in which graphite previously ignited *in vacuo* was used. The lampblack was deposited only on the end of the grid away from the filament, in order to avoid so far as possible any thermal reaction.

The apparatus used is shown diagrammatically in Fig. 1. Within the tube all metal parts are of platinum except for the short lengths of tungsten wire used to bring the leads through the glass. Attempts to protect the tungsten wires from the action of oxygen by plating them with gold were unsuccessful. The source of electrons is the calcium oxide coated filament F, operating on a potential drop of about 2 volts. Around this is a cylindrical electrode, G_1, with a circular grid of 50-mesh gauze 0.1 cm. from the filament. The next electrode is also cylindrical and has in the end a circular grid, G_2, of the same mesh as G_1. The distance from G_1 to G_2 is about 4 cm. One millimeter behind G_2 is the plate P.

The electrical connections are shown in the diagram; I_1, I_2, I_3 and I_4 are galvanometers. The potential P between filament F and grid G_1 is established by means of a storage battery and resistance in parallel. It is calculated by the expression

$$P = \frac{R_1}{R_1 + R_2}(E_1 - I_1R_2)$$

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[2] For a complete discussion of these methods see Franck and Jordan, "Anregung von Quantensprüngen durch Stosse," Springer, Leipzig, 1927.

Here R_1 and R_2 are the resistances indicated in the diagram, E_1 is the potential of the battery and I_1 is the current between the filament and the first electrode.

A connecting tube leads from the apparatus to the Pirani gage A, which consists of a fine platinum wire about 18 cm. long and 0.003 cm. in diameter. In the original experiments the wire was sealed in a straight glass tube 0.5 cm. in diameter. This form, while quite sensitive, was undesirable since when heated the wire became slack so that its position with respect to the walls, and hence the heat conductivity and apparent pressure, were variable. These difficulties were avoided by the arrangement shown in Fig. 1 in which the wire is stretched and centered by a small weight sliding in a glass tube. To maintain the walls at constant temperature the tube containing the wire was placed in a thermos bottle filled with water. The slight heating due to the Pirani wire did not raise the temperature of the water appreciably. The connections are shown in the figure and are those recommended by Campbell.[3] The Pirani wire is in one arm of a Wheatstone bridge the other three resistances of which are fixed. The voltage, V, necessary to balance the bridge is then a measure of the pressure. Over the pressure ranges for which the instrument was used (0.01 to 0.3 mm.) the pressure is a nearly linear function of $V^2 - V_0^2$, where V_0 is the voltage to balance the bridge when the pressure is negligible. If absolute pressure measurements are desired, the gage must be calibrated against a McLeod gage with each gas used.

Another connecting tube leads from the apparatus to a liquid-air trap, a mercury cut-off, devices for introducing various gases, a McLeod gage, another mercury cut-off and the pumps.

To prevent changes in pressure due to changes in temperature the electron tube was surrounded by a water jacket through which a stream of tap water was passed.

Procedure.—In general the current, potential and rate of reaction measurements were not taken simultaneously owing to the large number of instruments to be read. In making the rate of reaction runs the apparatus was pumped out to about 10^{-5} mm., the filament lighted and the trap at the tube immersed in liquid air. The gas was introduced, pressures being read both on the McLeod gage and the Pirani gage. The mercury cut-off at the tube was then closed and the rate of pressure change determined with various accelerating voltages between the filament and the first grid. These rates were followed by measuring the rate of deflection of the galvanometer I_4 when the bridge was balanced. Using a sensitive galvanometer changes of pressure of 10^{-5} mm. caused deflections of 1 cm.

In making the current-potential runs the method of Franck[2] was used. The oxygen was admitted as above and the plate current was measured with various accelerating potentials between the filament and the first grid, G_1. In most of the experiments a slight accelerating field of about 0.1 volt was maintained between G_1 and G_2 and a retarding field of 2.5 volts between G_2 and the plate, P.

A great deal of difficulty was encountered in obtaining sufficient electron emission to produce measurable chemical effects. In some cases the emission of a filament in oxygen gas was less than one-hundredth of its value in hydrogen.

Results of the Current-Potential Experiments.—The results of the current-potential measurements will be presented first. Fig. 2 shows a curve obtained with oxygen at 0.4-mm. pressure and is the graph of Expt. 1. The accelerating voltages (uncorrected, even for I_1) between the filament and the grid G are plotted as abscissas and the plate currents in arbitrary units as ordinates. Two breaks in the curve are apparent, a small one at about 9 volts (uncorrected) and a very pronounced one at about 12.5 volts

[3] Campbell, *Proc. Phys. Soc. London,* **33, 287** *(1921).*

(uncorrected). All of the curves in which the oxygen pressure was greater than 0.1 mm. show these two breaks but their relative magnitude varies. At high pressure the second predominates markedly, but as the pressure becomes lower it diminishes in magnitude and finally at the lowest pressures investigated has disappeared entirely, as may be seen in Fig. 3, which is the graph of Expt. 8 made at 0.05 mm.

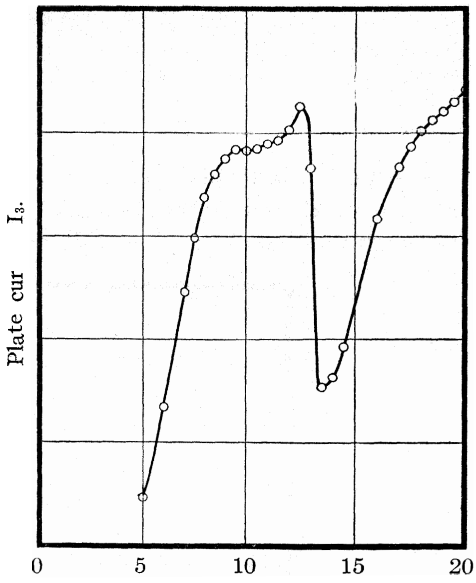

Fig. 2.

The results of all the current potential runs are summarized in Table I. The first line gives the experiment number; the second, the pressure of oxygen in millimeters of mercury; and the third and fourth give the values of the potential in volts (corrected) at which the first and second breaks occur.

The corrected voltages were obtained as follows. The true potential of the grid was determined by the equation given earlier. This is, however, not a true measure of the energy of the electrons since some energy is required to remove the electrons from the filament. This initial velocity correction was determined by taking the voltage at the foot of the curve obtained by plotting the values of the total emission against the voltage, in the region from 0 to 3 volts. The average of three determinations gave 0.9 volt for this correction. Subtracting this value from the applied potential gives for practical purposes the maximum voltage of the electrons and is spoken of as the corrected voltage. The maximum value is of interest rather than the average, which is about a volt lower, since the critical voltage is taken as the point where the cur-

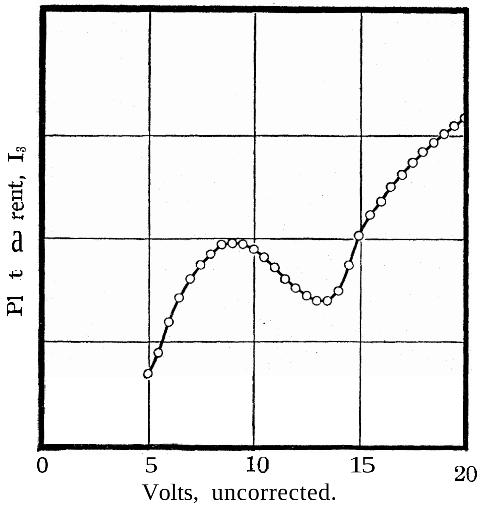

Fig. 3.

rent first starts to change, which is the point at which the fastest electrons just attain the critical voltage.

TABLE I

RESULTS OF CURRENT POTENTIAL RUNS

Experiment	1	2	3	4	5	6	7	8	9	
Pressure	0.40	0.32	0.28	0.22	0.18	0.11	0.08	0.05	0.05	
First break	8.1	7.8	7.5	7.9	7.9	7.6	8.2	7.9	8.2	Mean **7.9**
Second break	10.7	10.7	10.2	10.5	10.5	10.8	Not measurable			Mean 10.6

Results **of the** Rate Experiments.—The experiments on the rate of reaction proved definitely that bombardment with electrons having energies in the neighborhood of the previously-determined critical potentials produced an active form of oxygen capable of reacting with carbon to form carbon dioxide. However, it is not possible to fix accurately the potential at which reaction begins. This is due mainly to the poor emission of the filament in oxygen, which means that the rate of reaction is so low that it cannot be determined accurately. In order to obtain sufficient emission to work with, the filament must be large and must run at as high a temperature as possible. As a result of this the electron distribution is poor and the curves instead of breaking sharply when the critical potential is reached, bend gradually over a considerable voltage range. The fact that the oxygen molecule shows an affinity toward electrons also spoils the electron distribution. Another difficulty arose from the fact that when the filament was lighted a pressure decrease began although no accelerating potential was applied. Attempts to remove this zero rate by running for some time with high oxygen pressure and by cooling the tube failed, but since this zero

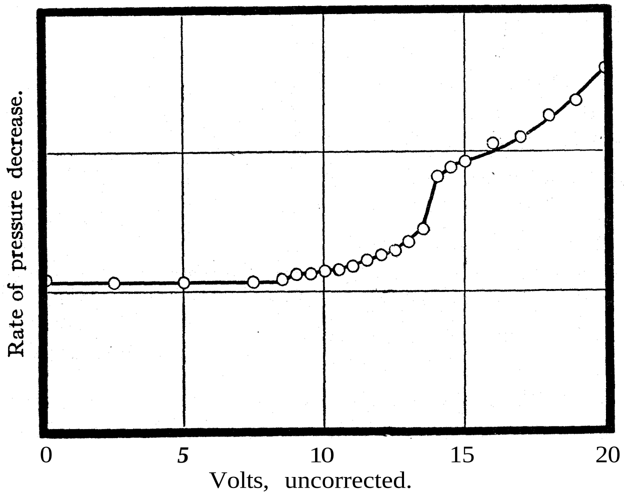

Fig. 4.

rate proved to be fairly constant it was possible to study the superimposed electronic effect.

Figure 4 shows a graph of Run 10 made at a pressure of 0.3 mm. The accelerating voltages (uncorrected) between the filament and G_1 are plotted as abscissas and the rate of pressure decrease in arbitrary units as ordinates. In this case two breaks are clearly present, one at 8.5 volts (uncorrected) and the second at 13 volts (uncorrected). This is in fair agreement with the current-potential data, as will be seen by referring to Fig. 2. In fact, Expt. 10 was made immediately following Expt. 1, keeping everything as nearly the same as possible.

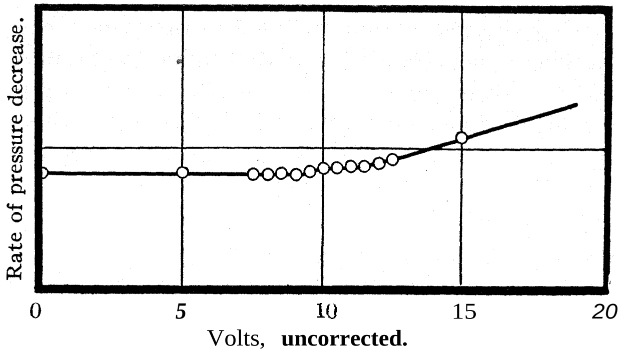

Fig. 5.

Here just as in the current-potential work if we go to low pressures the second break disappears. This is shown in Fig. 5, which is a graph of Run 15 made at 0.11-mm. pressure.

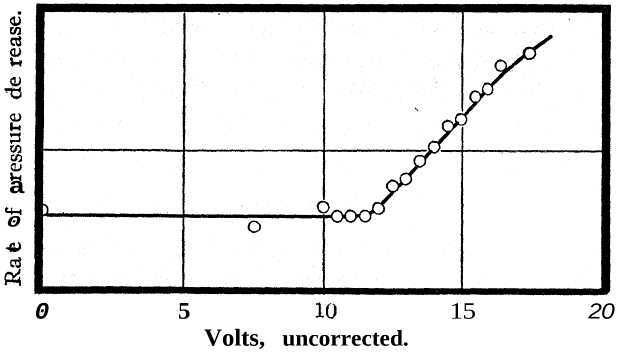

Fig. 6.

Experiments at intermediate pressures show in general only one break, which occurs at about the average of the two critical potentials determined in the current potential experiments. An illustration of this case is given in Fig. 6, which is a graph of Expt. 12 in which the oxygen pressure is 0.22

mm. The data from the most reliable reaction rate experiments are summarized in Table II. The first line gives the experiment number, the second the pressure of oxygen in millimeters of mercury, and the third and fourth give the voltages (corrected) at which breaks in the rate of reaction curves occur.

Table II

Reaction Rate Data

Experiment	10	11	12	13	14	15
Pressure	0.30	0.24	0.22	0.22	0.12	0.11
First break	7	9.3	9.1	9.2	<8.30	7.5
Second break	10.8	..	..	..	..	..

The earlier experiments are not included in the table since the readings were not taken near enough together to determine the point where a break occurs and since a more crude form of apparatus was then in use. They are not, however, in disagreement with the above results.

Considering the results of all the experiments it appears that at both the critical potentials observed an active form of oxygen is produced which reacts with the carbon.

The Reaction Product.—It is natural to suppose that the product of the reaction is carbon dioxide, since carbon monoxide will not be frozen out by liquid air at these pressures. The following experiments substantiated this supposition. The product from a number of runs was allowed to accumulate in the liquid-air trap, the residual oxygen was pumped out, the mercury cut-off at the pumps closed and the liquid air removed. A series of pressure readings was then made on the McLeod gage with the mercury at different heights. The product behaved as a perfect gas up to pressures of 18 cm. and so cannot have been water vapor. There was no permanent change in pressure on lighting the filament, which eliminates ozone as a possibility. Finally, some of the product was collected in a small side tube, cooled in liquid air, sealed off, and opened under barium hydroxide solution. A small quantity of a white precipitate of barium carbonate was obtained. l'hus the product must consist at least in a large part of carbon dioxide.

Discussion

It is interesting to compare the values of the critical potentials found with the known energy levels of oxygen. The band spectra of oxygen have been only partially worked out. There are electronic levels at about 1.7 volts and at 6 volts.[4] It is thought that the convergence limit of the oscillational states of the 6-volt electronic level corresponds to the energy for dissociation into two normal atoms. This gives about 7 volts for the work of dissociation of the normal molecule. Above 6 volts there are no levels given till ionization into O_2^+ between 14 and 15 volts. Thus spectroscopi-

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[4] Birge, *Bull. Nat.* Res. Council, 57, 244 (1926).

cally there are no energy levels yet given in the neighborhood of 7.9 or 10.6, though it is probable that such exist.

The work of various investigators on the determination of the critical potentials of oxygen by electron impact methods is not in good agreement. For the first critical potential, values varying from 7.9 to 0.2 volts have been reported.[5] However, the later work, which is probably more reliable, gives values close to 8 volts. A second critical potential is found by most observers at about 15.5 volts and is accepted as the ionization potential.[6]

Thus the first potential found in the present work is in good agreement with previous values and is apparently a resonance potential of the oxygen molecule. The second potential and its peculiar dependence on the pressure cannot be interpreted with any certainty, but some possibilities may be considered. Perhaps the simplest explanation is that we are dealing with a previously unrecorded critical potential of the molecule, but this would give no reason for such a marked dependence on the pressure. Or it might be that the second potential represented dissociation of the molecule into a normal and an excited atom. Since dissociation to normal atoms requires 7 volts, that leaves 3.6 volts for the atomic excitation. It seems probable from the study of the auroral lines that there is an atomic level in this region. Another explanation might be that the second break is due to carbon dioxide, which is reported as having a resonance potential at *10.0* volts.[7] This would account for the variation with the pressure since at low oxygen pressures the carbon dioxide would diffuse rapidly to the liquid-air trap while at higher pressures its removal would be retarded. This hypothesis would also account for the fact that previous potential work in oxygen has not in general revealed a critical point at *10.6* volts. It would require, on the other hand, that inelastic collisions of electrons with carbon dioxide be much more efficient than those with oxygen.

The author wishes to express his thanks to Professor Tolman, to Dr. Baxter, and especially to Dr. Glockler, for their assistance in this research; also to the Carnegie Institution of Washington for financial aid received through a grant made to Professor A. A. Noyes.

Summary

The critical potentials of oxygen gas have been determined at various pressures. In addition to the value of 7.9 volts which has been found by previous experimenters, a second critical value was found at *10.G* volts. The latter appears distinctly only at pressures above *0.1* mm., but becomes very pronounced at pressures of *0.2* to 0.4 mm.

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[5] Foote and Mohler, Bureau of Standards Publication No. 400, 1920; Boucher, *Phys. Rev.*, 19, 202 (1922); Franck and Hertz, *Verh. deut. physik. Ges.*, 15, 34 (1913); Hughes and Dixon, *Phys. Rev.*, 10, 502 (1917).

[6] *H. D.* Smyth, *Proc. Roy. Soc. London*, **105A,** 116 (1924).

[7] Mackay, *Phys.* ***Rev.,*** 24, 319 (1924).

The reactivity toward carbon of oxygen gas excited by electron impact was studied. There was no reaction below 7.9 volts, but between 7.9 and 10.6 volts a reaction commenced and increased in rapidity up to the highest potentials investigated. The product of the reaction is carbon dioxide, at least in large part.

PASADENA, CALIFORNIA

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

THE HEATS OF DISSOCIATION OF THE MOLECULES, CH, NH, OH AND HF

BY DONALD STATLER VILLARS

RECEIVED MARCH 22, 1929 PUBLISHED AUGUST 7, 1929

In an investigation on the dissociation energetics of the molecule of hydrogen cyanide, it was necessary to make an estimate of the heats of dissociation of its different possible decomposition products. Although it sounds strange to the chemist to speak of the molecules, CH, NH and OH, still their existence is definitely proved by the observation of band spectra[1] which are ascribed to them. The molecules, unsaturated chemically, are most probably extremely reactive, but we should not consider them unstable, in the sense that they have a tendency to decompose. The knowledge of the heats of dissociation of these molecules has great theoretical importance in studying the dissociation of other compounds, as well as hydrogen cyanide.

In order to calculate these heats, I have made use of two empirical principles discovered by band spectroscopists. First, Kuhn[2] has shown that the restoring force constant, C, in the equation for the vibration of a harmonic oscillator is approximately proportional to the heat of dissociation of the molecule.

$$C \equiv \mu\omega_0^2 = kD \qquad (1)$$

ω_0 is the frequency of vibration for infinitely small displacement and is determined experimentally by the difference between the first and second vibrational energy levels of the molecule as measured from its band spectrum; μ is the resultant mass and equals $m_1m_2/(m_1 + m_2)$ for a diatomic molecule. Second, Mecke[3] has shown that molecular constants vary with the atomic number in much the same manner as other physical and chemical constants. The method of estimation, then, is to determine

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[1] CH: Heurlinger and Hulthén, *Z. wiss. Phot.*, 18, 241 (1919); *Compt. rend.*, 173, 524 (1921); *Z. Physik*, 11, 254 (1922). NH: Hulthén and Nakamura, *Nature*, 119, 255 (1927). OH: Grebe and Holtz, *Ann. Physik*, 39, 1243 (1912); Heurlinger, "Dissertation," Lund, 1918; Fortrat, *J. phys.*, 5, 20 (1924); Jack, *Proc. Roy. Soc. London*, **115A**, 373 (1927); **118A**, 647 (1928).

[2] Kuhn, *Z. Physik*, 39, 77 (1926).

[3] Mecke, *Physik. Z.*, 28, 483 (1927).

k in (1) and to calculate D from this, making use of ω_0, obtained already or interpolated by applying Mecke's principle.

Birge[4] gives the following values of ω_0 which he calculated for the molecules CH, OH and HF: ω_0'' HF, 3962 cm.$^{-1}$; OH, 3570 cm.$^{-1}$; CH, 2797 cm.$^{-1}$. Interpolating for ω_0 of NH gives 3188 cm.$^{-1}$. Figure 1 shows that all of the points lie on a perfectly straight line.

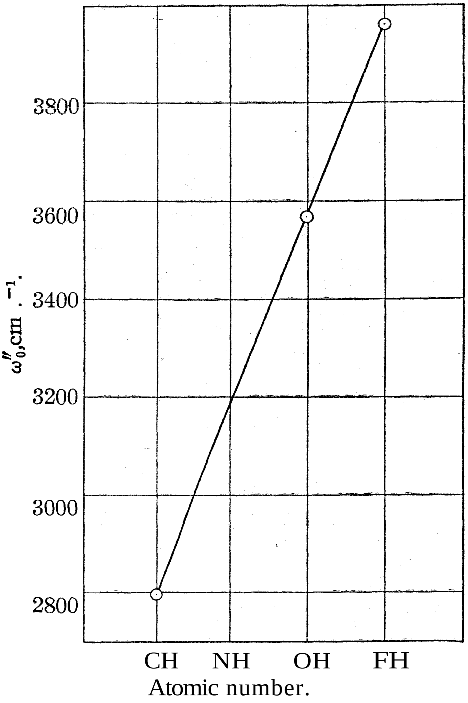

Fig. 1.

The next step made in the approximation process is to tabulate C and D (see Equation 1) for several different molecules and to calculate therefrom the proportionality constant, k. This is given in Table I, the values in parentheses being the results of estimation. It will be immediately evident that k varies also with the atomic number for the similar molecules, H_2, HCl, HBr. Plotting k against atomic number in Fig. 2, we may interpolate and get the values given in parentheses under k. Knowing k and ω_0, one may immediately calculate D and this, too, is given in Table I. If this interpolation is justified, it can be seen that the error involved in our value of D is at most not over 3%.

We can compare these calculated heats of dissociation with some quasi-experimental ones which may be obtained from the work of Ellis.[5] According to him, the bonding power (C in the above notation) of the C–H

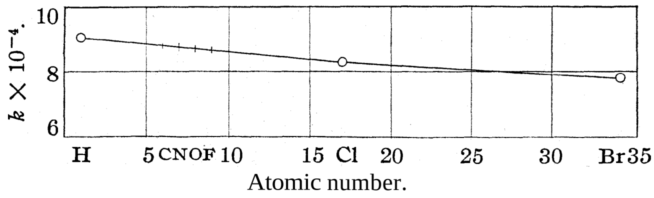

Fig. 2.

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[4] Birge, "Molecular Spectra in Gases," *Bulletin National Research Council,* **Washington,** D. **C., 11,** No. **57,** 230 (1926).

[5] Ellis, *Phys. Rev.,* **33,** 35 (1929).

TABLE I

HEAT OF DISSOCIATION

Molecule	μ	ω_0, cm.$^{-1}$	D Volts	Kilocal.	k
Cl_2	17.73	555	2.5	58.5	9.36×10^4
Br_2	39.95	326	2.0	45.2	9.42
I_2	63.45	214	1.5	35.2	8.14
N_2	7.00	2345	9.5	219.0	17.6
NO	7.46	1892	7.3	169.0	15.86
CO	6.85	2150	11.2	268.0	12.3
CN	6.47	2060	9.5	219.0	12.1
H_2	0.50	4264	4.4	101.0	9.10
CH	.923	2797	(3.55)	(82.0)	(8.81)
NH	.933	3188	(4.65)	(108.3)	(8.76)
OH	.942	3570	(5.98)	(138.0)	(8.71)
HF	.950	3962	..	(172.0)	(8.68)
HCl	.972	2941	4.4	101.7	8.29
HBr	.976	2559	..	81.7	7.82

linkage is 23% greater in hexane (heat of dissociation, 97 kilocal.) than in the CH molecule. If C is proportional to the heat of dissociation, D, then

$$\frac{C_1}{C_2} = 1.23 = \frac{k_1 D_1}{k_2 D_2} = \frac{97}{D_{\mathrm{CH}}} \qquad (2)$$

where the subscripts 1 and 2 refer to hexane and CH, respectively. If we neglect the fact that k_1 (9.15) is different from k_2 (8.81 according to Table I) we can calculate D_{CH}

$$D_{\mathrm{CH}} = 79 \text{ kilocal.}$$

which agrees very well with the value 82 kilocal. obtained above. To say that the ratio $k_1/k_2 = 1$ is, of course, inconsistent with our other method of calculation and any results obtained in this manner can only indicate the order of magnitude. Likewise, an application of Equation 2 with the same assumption concerning the ratio k_1/k_2 gives us a value for the heat of dissociation of Cl_3C–H. Using Ellis' data for ω_0, this is found to be 105 kilocal., which agrees with his observed value of 108 kilocal.

Mlis also obtained values for the linkage heat of the N–H bond. In aniline he reports it as being 113 (±15%) kilocal. He compared this spectroscopic value with a chemical value obtained by dividing the "atomic" heat of formation (referred to the gaseous atoms) of ammonia by three. He found 101 kilocal. but this should be **93** if we accept the new value[6] for the heat of dissociation of nitrogen, $D_{N_2} = 9.5$ volts or 219 kilocal. This checks well the value obtained from Equation 2 (*i.* e., 91.4 kilocal.)

$$\frac{3440^2 \times 0.989}{3188^2 \times 0.933} = \frac{k_a\, 113}{k_{\mathrm{NH}}\, D_{\mathrm{NH}}}$$

$$D_{\mathrm{NH}} = 91.4 \text{ kilocal. or } 4.0 \text{ volts if } k_a/k_{\mathrm{NH}} = 1$$

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[6] Mulliken, Phys. Rev., 32,761 (1928); Birge, Nature, 122,842 (1928).

Here $k_a = 10.36$ and the discrepancy may be ascribed to its difference from k_{NH}.

In view of the above discussion concerning the empirical variation of k with atomic number, it seems best to choose as values 'for D those given in Table I.

The heat of dissociation of CN has already been calculated to be 9.5 volts[7] (1 volt = 23 kilocal.). Recent work has indicated that it is probable that one of the products of this dissociation is an excited atom.[6] If it is a characteristic of odd molecules that their normal states will dissociate, resulting in an excited atom, while their next excited molecular states dissociate into normal atoms,[8] then some doubt is thrown on the meaning of our above value for D_{CH}, as it must represent only an upper limit for the heat of dissociation into *normal* atoms. As yet there has been no evidence advanced that this is true for the hydride molecules under consideration.[9] However, even were this true, we still have obtained the *actual* energy necessary to break up the molecule, a quantity which has very interesting theoretical implications.

Our value for the heat of dissociation of OH agrees in order of magnitude with other existent data. If the "atomic" heat of formation of water is 238.8 kilocal., then the heat of dissociation of water into H and OH is $238.8 - 138 = 100.8$. Senftleben and Rehren[10] estimate it to be less than 112 kilocal. Bonhoeffer and Reichardtu obtain a value in agreement with theirs. Bates and Taylor[12] find that the efficiency of excited mercury (113 kilocal.) is much less in its dissociation of water vapor than in its action on other molecules. An explanation, accessory to that advanced by Bates and Taylor, might be that the amount of energy available from the mercury is in excess of that necessary to dissociate the water molecule by 12 kilocal, and that we have here a resonance phenomenon such as is observed elsewhere in collisions of the second kind.[13]

Summary

Data from band spectra have been interpolated by Mecke's method and the magnitude of the heat of dissociation of the molecules, CH, NH, OH and HF was calculated to be, respectively, 82.0, 108.3, 138.0 and 172 kilocalories.

URBANA, ILLINOIS

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[7] Mulliken, *Phys. Rev.*, 32, 206 (1928).

[8] Heitler and Herzberg, Z. *Physik*, 53, *52* (1929).

[9] Cf. Mulliken, *Phys.* ***Rev.***, 33, 738 (1929), Table I.

[10] Senftleben and Rehren, Z. *Physik*, 37, 529 (1926).

[11] Bonhoeffer and Reichardt, *Z. Elektrochem.*, 34, 652 *(1928)*; *Z. physik. Chem.*, 139, 92 (1928).

[12] Bates and Taylor, THIS JOURNAL, 49,2450 (1927).

[13] Beutler and Josephy, *Naturwissenschaften*, 15, 540 (1927); Webb and Wang, *Phys. Rev.*, 33, 329 (1929).

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

A NEW DIFFERENTIAL PRESSURE GAGE

BY A. R. OLSON AND L. L. HIRST

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In a recent investigation we found it necessary to follow the speed of a very slow gas reaction by means of the pressure change produced in the reacting mixture. In this investigation it was desirable to work at about atmospheric pressure. The differential gage devised by Frank,[1] in which he combined the circuit developed by Gunn[2] with a condenser, one plate of which was mounted on the thin glass diaphragm of a reaction chamber, would have been satisfactory. This circuit, however, is complicated and very sensitive to small battery variations, since it depends upon current measurements.

Within the past ten years piezo-electric quartz crystals have been introduced into radio circuits to hold the frequency constant.[3] By combining such a crystal-controlled oscillator with a resonance circuit which utilized a condenser mounted on a glass diaphragm, we were able to construct a gage which combined the advantages of simplicity and accuracy.

The wiring diagram of the oscillation and resonance circuits[4] is shown in Fig. 1. We used a 301 A Cunningham tube operated with a 6-volt filament battery and a 150-volt plate battery. Q is quartz plate which has frequencies of 1080 and 1211 K. C. The inductance L_1 has 25 turns of No. 14 copper wire wound on an 11-cm. bakelite cylinder. L_2 in the resonance circuit consists of 80 turns of No. 16 wire wound on an 8.5-cm. bakelite cylinder. It is tapped at every turn to facilitate adjustment. C_1 is a standard $1500\mu\mu$ variable condenser; C_2 is a small parallel plate condenser which is shown in detail in Fig. 2. The diaphragm D is a No. 0 cover glass about two inches in diameter, to which the lower condenser plate is attached by shellac. The cover glass was attached to the tube by sealing wax. In case an all-glass system is needed, the diaphragm can be blown from the tube itself. The upper plate is rigidly fixed to the top of the gage by an adjusting screw. The distance between plates is about 0.3 mm.

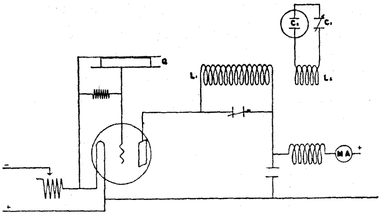

Fig. 1.

When circuit is oscillating, the plate current is about 15 m.a., as shown by the meter MA, Fig. 1. When resonance is established in the gage circuit, the plate current increases very sharply by about 10 m.a. To adjust the apparatus, the oscillator is set going, C_1 is fixed at a rather large value ($1000\mu\mu$ to $2000\mu\mu$) and L_2 is varied until resonance is obtained. No further adjustments are necessary. For accurate work

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[1] H. S. Frank, unpublished Thesis, University of California.

[2] Gunn, *Phil.* Mag., 48, 224 (1924).

[3] W. G. Cady, *Proc. last. Radio Eag.*, 10, **83** (1922); G. W. Pierce, *ibid.*, 15, 9 **(1927).**

[4] See Catalog E, General Radio Co., Cambridge, **Mass.**

it is desirable to thermostat the whole circuit to prevent capacity changes, etc., during the measurements.

To use the gage, fill one side with the reacting mixture, and the other side with an inert gas. A small leveling bulb will help to adjust the pressure until the diaphragm is in its undisplaced position. Then start the oscillator and increase C_1 until the sharp increase in the plate current is obtained. Decrease C_1 again until oscillation is restored and repeat the operation. Since the frequency of the oscillator is constant and since the inductances L_1 and L_2 are fixed, the total capacity in the resonance circuit is fixed But $1/C = 1/C_1 + 1/C_2 =$ a constant. Therefore $dC_1/dC_2 = -C_1^2/C_2^2$, or the ratio of the changes of capacity is directly proportional to the square of the ratio of their absolute values. For the condition as outlined above, a small change in C_2 corresponds to a large change in C_1. In our work the gage was reproducible to one division of our standard condenser, which corresponded to 3×10^{-4} mm. mercury pressure. This does not represent the limit of reproducibility of the electrical circuit, for when C_2 was replaced by a small fixed condenser, C_1 readings checked within such limits that we could estimate fractions of a subdivision, *i. e.*, tenths of a division.

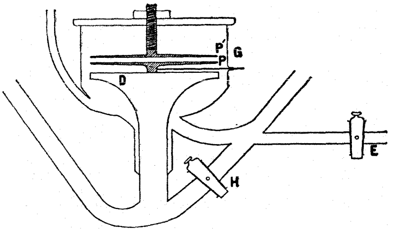

Fig. 2.

To calibrate the apparatus various methods can be used. Thus both sides can be filled with an inert gas and then the pressure on one side can be changed a given amount by changing the leveling bulb, or the whole apparatus may be evacuated and a liquid with a known pressure introduced on one side. The details of such a calibration can be seen from the following data

Press above D, cm. of Hg	**24 5**	**24 5**	$17\ 1 \times 10^{-3}$	$17\ 1 \times 10^{-3}$	$17\ 1 \times 10^{-3}$	17.1×10^{-3}
Press. below D, cm of Hg	**24 5**	**24 5**	$17\ 1 \times 10^{-3}$	$17\ 1 \times 10^{-3}$	$14\ 6 \times 10^{-3}$	$14\ 6 \times 10^{-3}$
C_1	**1026 8**	**1026 9**	**1028 8**	**1028 8**	**1007 7**	**1007.8**

A change of pressure on both sides of D from 24.5 cm. to 2 X 10^{-3} cm. produced a change in C_1 of only two divisions. If the pressure on one side is kept constant, and the pressure on the other side of D is changed, C_1 changes approximately one division for each thousandth millimeter change of pressure. If C_1 were adjusted so as to resonate at $2000\mu\mu$, the change in C_1 would be about four times as much.

Summary

A new simple and accurate differential pressure gage has been devised which will permit the study of very slow reactions at any pressure even when an all-glass gage is needed.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

SOME APPLICATIONS OF ELECTRIC MOMENTS TO ELECTRONIC THEORIES OF VALENCE

BY CHARLES P. SMYTH

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As most of the electronic theories of valence in their application to organic compounds involve the idea of polarity as a controlling factor, it would seem logical to use the measure of molecular polarity, that is, the electric moment of the molecule, as a means of examining the validity of the theories. In the hands of many workers with these theories, the signs of positive and negative charges and the circles or dots representing electrons have gradually lost all physical significance and become mere symbols of chemical behavior. To attempt to apply principles of electrostatics to test these molecular formulas would be idle. However, hypotheses which have been developed on the basis of physical laws lend themselves to examination in the light of the electric moments of the molecules to which they are applied, provided that the molecules are not too complex.[1] It is not generally possible to accept or reject unreservedly an hypothesis on the basis of the electric moment of the molecule of a single substance or even of three or four substances, although strong evidence pro or con may be obtained. One may, however, set definite physical limitations upon the polarities supposed by the hypotheses and, at the same time, consider the limitations of the electric moment as a criterion by which these hypotheses may be judged.

In view of the uncertainty and the rapidity of change in the hypotheses of atomic structure and our ignorance of the fundamental nature of the chemical bond, it is impossible to assign definite electronic arrangements to the atoms in a molecule. It is generally believed, however, that a single chemical bond involves a pair of electrons and the electrostatic effect of their charges is represented by picturing certain locations between the linked atomic nuclei as occupied by the electrons. The consideration of these locations makes possible the discussion of the distribution of the electricity in the molecule.

In an electrically symmetrical molecule the center of gravity of the electrons coincides with the electrical center of gravity of the positive charges and the molecule has no electric moment. If the electrostatically effective position of an electron is displaced through a distance d, an electric doublet is created and the molecule now possesses an electric moment equal to the electronic charge, $4.774 \times 10^{-10} \times d$. The symmetrical tetrahedral structure commonly ascribed to methane should have

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[1] For an explanation of electric moment and its relation to molecular structure, see Smyth, *Phil. Mag.*, 47, 530 (1924); THIS JOURNAL, 46, 2151 (1924).

no electric moment, but it is highly improbable that the unsymmetrical pyramidal structure attributed by Henri to methane should not possess a moment.[2] The relation of the theory of a pyramidal carbon atom to the electric moments of tetra-substituted methane molecules has been discussed by Weissenberg[3] and by Ebert and von Hartel.[4] As Sänger[5] has found zero electric moment for the methane molecule, the usually accepted picture of a symmetrical structure appears justified.

The theory of alternating polarities has received much adverse criticisni on chemical grounds and the supposed physical evidence of alternation given by melting points, heats of combustion, etc., has been shown to afford no proof of any intramolecular alternation of polarity.[6] The theory as proposed by Cuy[7] requires that, even in the paraffins, the carbons of the chain should be alternately positive and negative. The difference in polarity between the two carbons in ethane should give rise to an electric doublet, but no moment is found for the ethane molecule? Although, because of the alternation and consequent canceling of the polarities, there should be no building up of large moments in the higher members of the series, there should certainly be moments in the molecules of many and differences should exist between adjacent members. n-Hexane and n-heptane have been shown to be without moment,[9] as have also the other isomers of heptane and one octane. If any alternation in polarity occurred, it would be impossible that all of these molecules should be electrically symmetrical. Further evidence against an alternation in polarity is given by the absence of any difference in moment among the higher members of other homologous series to be considered presently.

The differences between the polarizations of the isomers of heptane were shown by Smyth and Stoops to be so small that the largest difference would, if due to but one pair of electrons, correspond to a displacement of the effective position of the charges of less than 3×10^{-11} cm. from a symmetrical location, that is, approximately 0.002 of the distance between the carbon nuclei in the chain. This distance was calculated as an upper limit for the displacement. Actually, such differences in polarization as were observed might easily occur without any lack of electric symmetry in the molecules. Hydrocarbon molecules may be resolved into various

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[2] Henri, *Chem. Rev.*, 4, 189 (1927).

[3] Weissenberg, *Naturwissenschaften*, **15**, 662 (1927).

[4] Ebert and von Hartel, *ibid.*, 15, 668 (1927).

[5] Sänger, *Physik. Z.*, 27, 556 (1926).

[6] Kharasch and Darkis, *Chem. Rev.*, 5, 571 (1928); Carothers, THIS JOURNAL, 46,2226 (1924).

[7] Cuy, *ibid.*, 42, 503 (1920).

[8] Smyth and Zahn, *ibid.*, 47,2501 (1925).

[9] Smyth and Morgan, *ibid.*, **50**, 1547 (1928); Smyth and Stoops, *ibid.*, **50**, 1883 (1928).

alkyl radicals to which it is customary to assign varying degrees of electronegativity, Thus Lucas, Simpson and Carter[10] state that, in propane, due to the fact that hydrogen exerts a stronger pull on electrons than methyl does, the electron pairs joining the central carbon to hydrogens are presumably not so firmly held by the carbon so that the polarities of all the carbon–hydrogen unions in propane are not the same, hydrogen joined to the secondary carbon being more negative than hydrogen joined to a primary carbon. If the carbon linkages are tetrahedrally arranged, this difference in the polarities would make the molecule electrically unsymmetrical. A greater effect should be produced at the central carbon of n-heptane, as the two propyl groups attached to it are supposed to be less electronegative than the methyl groups on the central carbon of propane, but n-heptane is found to possess no detectable moment. It is unnecessary to make any assumption of tetrahedral linkages in order to conclude that the differently distributed groups in the isomers of heptane would give rise to electrical unsymmetry if their supposedly different electronegativities actually involved appreciably different displacements of their bonding electron pairs. The previously given calculation shows how small these displacements must be, if they exist at all. The electrical behavior of the paraffins thus gives no support to the hypothesis that the alkyl groups possess electronegativities which vary with the distance of the binding electron pair from the α-carbon.

It would appear, however, that the attachment of very strongly electronegative groups to the alkyl radicals should cause greater electron displacements and accentuate the differences between the radicals. When the hydroxyl is attached to an alkyl radical to form an alcohol, a strong electric moment results. In considering the dielectric constants of methyl, ethyl and propyl alcohols, Thomson[11] has pointed out that the intense electric field due to the principal moment of the molecule might be expected to give rise by induction on the rest of the molecule to moments of the same sign as the original moment, thus increasing the moment of the molecule as a whole. The increase in the moment of the molecule due to these small moments resulting from electronic displacement would be greater, the greater the length of the carbon chain. What appeared to be evidence of such a small increase with increasing length of the carbon chain was obtained by the writer[1] in calculating the moments of several alcohols and in other series as well, but it now seems probable that, at least in the alcohols and ketones, the apparent small increase in moment with increasing size of the molecule was due to error caused by molecular association. The strong molecular association of the alcohols and water makes their moments difficult to determine with accuracy, but the most recent values

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[10] Lucas, Simpson and Carter, THIS JOURNAL, 47,1462 (1925).

[11] Thomson, *Phil.* Mag., 46,497 **(1923).**

lie within 0.15×10^{-18} of 1.7×10^{-18} and show no regular variation with increase in the length of the chain.[12] It is evident that there are no very great differences among the displacements of the bonding electron pairs in the different alkyl groups in the alcohols.

More satisfactory conclusions may be drawn from the moments of the halides, which are less affected by. molecular association and are not complicated by the presence of two doublets in the molecule as is the case with the alcohols.

TABLE I

ELECTRIC MOMENTS OF THE HALIDES $\times 10^{18}$

	X = Cl		Br	I
HX	1.03(1)		0.79(1)	0.38(1)
CH_3X	1.59(2)			1.62(3)
C_2H_5X	1.98(2)		1.86(4)	1.66(5)
C_4H_9X	1.89(6)		1.87(6)	
$C_7H_{15}X$			1.86(6)	
C_6H_5X	1.52(4)		1.57(7)	
cis-CHX=CHX	1.85(8)		1.22(8)	0.75(8)
trans-CHX=CHX			0(8)	0(8)
cis-CHCl=CHBr		1.54(8)		
trans-CHCl=CHBr		0(8)		
CH_2=CCl_2	1.18(8)			

(1) Zahn, Phys. Rev., 24, 400 (1924); (2) Sircar, *Indian* J. Phys., 12, 197 (1928); (3) Mahanti and Sen Gupta, *ibid.*, 12, 191 (1928); (4) Smyth and Morgan, THIS JOURNAL, 50, 1547 (1928); (5) Unpublished work of Dr. W. N. Stoops; (6) Unpublished work of Mr. H. E. Rogers; (7) Williams, Physik *Z.*, 29, 683 (1928); (8) Errera, Physik. *Z.*, 27, 764 (1926).

In the molecules of these halides the negative end of the electric doublet is toward the halogen. Consequently, the more electronegative the group attached to the halogen, that is, the more strongly it draws the binding electron pair toward itself, the shorter is the distance between the centers of gravity of the positive and negative electricity and the smaller the moment. This works out quite satisfactorily for hydrogen, methyl and ethyl chlorides, in which the moment increases as the supposed electronegativity decreases. The difference between ethyl chloride and butyl chloride is no greater than the combined probable errors in the values. An accurate value for methyl bromide is lacking, but approximate values calculated by Höjendahl[13] show that the moment of methyl bromide is about 0.25×10^{-18} lower than that of ethyl bromide. The supposed differences in electronegativity of the bromides and iodides, as in the case of the chlorides, accord well with the increase in moment from hydrogen to ethyl. Beyond this, however, no difference is apparent in the

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[12] Stranathan, Phys. Rev., 31, 653 (1928); Krchma and Williams, THIS JOURNAL, 49,2408 (1927); Williams, Physik. *Z.*, 29,204 (1928).

[13] Höjendahl, "Thesis," Copenhagen, 1928.

chlorides and bromides, data for the iodides being lacking. The moments of chlorobenzene and bromobenzene are much higher than those of the corresponding hydrogen halides, although the phenyl group is supposed to be more electronegative than hydrogen. The supposedly different electronegativities are thus only partially successful in explaining the differences in moment. It is evident that some effect is transmitted through the first two carbons of a chain, although the effect upon the second is small and, beyond the second, no effect is apparent in the electric moment.

It is of interest to contrast this transmission of an electrical effect through a chain with the effect of the chain upon the ionization constants of unsubstituted and halogenated fatty acids as quoted by Lowry[14] and by Kharasch and Darkis and shown in Table II.

TABLE II

IONIZATION CONSTANTS OF FATTY ACIDS ($\times 10^5$)

		α			β			γ			δ		
		Cl	Br	I	Cl	Br	I	Cl	Br	I	Cl	Br	I
HCOOH	21.4												
CH_3COOH	1.8	155	156	75									
CH_3CH_2COOH	1.4	147	108	90	8.6	9.8	9.0						
$CH_3(CH_2)_2COOH$	1.5	139	106		8.9								
$CH_3(CH_2)_3COOH$	1.6							3 0	2.6	**2.3**			
$CH_3(CH_2)_4COOH$	1.46										1.9	1.9	1.7

The constants for the unsubstituted acids in the second column of Table II show that, as in the case of the electric moments of the halides, lengthening of the hydrocarbon chain beyond two has little effect. The values for the halogenated acids are somewhat conflicting but, after a great drop in the effect upon the ionization when the halogen is moved from the first to the second carbon, the effect continues to diminish as the distance of the halogen from the carboxyl increases and is still noticeable in the δ-halogenated acid, where it has to be transmitted through five carbons and an oxygen. Yet, in the alkyl halides, no electronic shifts produced by halogen more than two carbons away can be detected by means of electric moments.

Wolf and Lederle[15] have found that the electric moments of a number of ketones, including methylhexyl ketone and methylnonyl ketone, differ from the value for acetone by no more than the experimental error. Their results give no evidence of any change in moment with increasing length of the hydrocarbon chain. There is thus no measurable electrostatic effect transmitted beyond the first carbons attached to the carbonyl group and no sign of any alternating polarity in the chains.

Electronic theories of valence have been applied very frequently to the double bond and, by many investigators, the bond between two carbon

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[14] Lowry, *Trans. Faraday Soc.*, 19, 497 (1923).

[15] Wolf and Lederle, *Physik. Z.*, **29**, 948 (1928).

atoms has been regarded as polar, one pair of electrons being shared between the two carbons and one of the carbons containing one more pair of electrons than the other. Smyth and Zahn[8] have found the electric moment of the ethylene molecule to be zero and have therefore concluded that no more than a small proportion of the ethylene molecules, if any, can he polar. It was further concluded that a molecule in which a single unpaired electron was held by each carbon should possess a moment and therefore could not exist in any considerable quantity in the ethylene. This conclusion is supported by the recent discovery of Vaidyanathan[16] that ethylene is diamagnetic instead of paramagnetic as previously supposed. The zero moment found experimentally for ethylene does not disprove the theory of Lowry[17] and of Carothers[6] that a very small fraction of the molecules containing a double bond are polar at the bond and that it is this small fraction which is active. The small moment, 0.37×10^{-18}, found for α-butylene may be due to the difference in the electronegativities of the hydrogen on one side of the doubly-bonded carbons and the ethyl on the other side as the electrons of the double bond are shown by the high refraction associated with them to be mobile and more easily displaceable than those in a single C–C bond.[18] The moment may, however, as suggested by Smyth and Zahn, be due to small electronic shifts induced in the ethyl group by the force field around the double bond.

If the double bond consisted essentially of a single electron pair held between the atoms and a second pair held by one atom or the other, as supposed in most theories of a polar double bond, the difference in freedom of rotation between singly and doubly linked atoms mould not be explained. This well-recognized difficulty, which has been discussed by Sidgwick,[19] is, of course, obvious in the problem of geometrical isomerism. The comparative rigidity of the double bond is brought out strikingly by the results of Errera for the moments of the acetylene dihalide molecules given in Table I, where the absence of moment in the trans-compound fits in admirably with the conventional representation of the double bond as formed by the sharing of an edge between two carbon tetrahedra. The doublets at the other imaginary tetrahedral apices thus brought into one plane would cancel one another in the trans-compounds so that the moments of the molecules would be zero. Any freedom of rotation about the band would tend to produce electrical dissymmetry and a resultant moment, as found in ethylene chloride, bromide and glycol, for which large moments have been calculated approximately.[18] One might wonder

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[16] Vaidyanathan, *Indian J.* Phys., 12, 165 (1928).

[17] Lowry, *Trans. Faraday Soc.*, 19,488 (1923); *J. Chem. Soc.*, 123,822 (1923).

[18] See Smyth, *Phil. Mag.*, 50,361 (1925).

[19] Sidgwick, *Trans. Faraday Soc.*, 19,469 (1923).

why the cis-compounds with the two halogen doublets reenforcing each other on the same side of the molecule do not have larger moments than the alkyl halides where there is only one halogen doublet. As was found in the chloromethanes and the dihalogenated benzenes,[20] the two halogen atoms repel each other, widening the angle between the axes of their doublets and decreasing the resultant moment of the molecule as a whole. The repulsion and consequent widening of the angle should be greater, the larger the halogen atoms, and it is evident that the moment is increasingly reduced on passing from chlorine to bromine to iodine. Purely geometrical considerations show that, when the two halogens are attached to the same tetrahedral carbon, the angle between their doublets is greater and the resultant moment less, as evidenced in the value for $CH_2{=}CCl_2$.

The rigidity of the doublet bond between carbon atoms is maintained in the structure proposed by Kharasch and Darkis[6] in which two pairs of electrons are shared between the two carbons, one pair being close to the carbon to which the less electronegative groups are attached and a definite polarity being postulated. This is neither proved nor disproved by the moments in Table II, but the zero moment found for ethylene shows the absence of any detectable polarity in this simple molecule, while the postulates of Kharasch and Darkis would lead us to expect a marked polarity. There appears to be no physical foundation for the postulate of Kharasch and Darkis that "the relative position of the second pair of valence electrons of the double bond depends upon the nature of radical attached to it in such a way that they are always on the carbon atom opposite to that carrying the most electronegative radicals." The more electronegative radicals draw their binding electron pairs farther away from the carbon to which they are attached, thus increasing the effective nuclear charge of this carbon. The increased charge should tend to shift any other adjacent electrons toward this carbon and thus increase very slightly the effective nuclear charge of the carbon away from which they have shifted. A mechanism of this general character is commonly assumed to explain the transmission of an effect through a chain. The short distance through which such an effect can be detected electrostatically has been pointed out. The postulate of Kharasch and Darkis requires that the electrons be forced away from the carbon with the higher effective nuclear charge toward that with the lower charge. However effective such a postulate may be in explaining chemical behavior, it appears electrostatically unsound.

When the results of Errera, Smyth and Morgan and Höjendahl[21] for the moments of substituted benzenes were found to be consistent with

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[20] Smyth, *Phil. Mag.*, 47, 530 (1924); Smyth and Morgan, THIS JOURNAL, 49, 1030 (1927); Errera, (8) Table I.

[21] Hojendahl, Nature, 117, 892 (1926).

the hypothesis of a benzene ring forming a plane hexagonal structure, it was thought that the relative electronegativities of radicals could be determined not only by comparing the electric moments of analogous compounds containing the different radicals but also by measuring the moments of molecules in which any two groups to be compared were placed opposite one another in the para-position.[20] Williams[22] has recently constructed a list showing the moments produced by the attachment of each of nine common radicals to the benzene ring. When two groups are in the para-positions, the resultant moment should be the difference of the two separate moments, the signs of the moments being taken into account. Although this relation has been found to hold approximately for many of the simple groups, marked deviations occur frequently when more complex groups are attached.[22,13] Particularly in the ortho- and meta-positions, the groups may attract or repel one another quite apart from their action through the carbons of the ring and the resulting effect upon the moment of the molecule is commonly much greater than any to be expected from electronic shifts in the carbon ring. The repulsive effects of this kind, which have been discussed by Smyth and Morgan[20] for the substituted benzenes, are similar to those occurring in the acetylene dihalides. Because of these large changes external to the ring, it seems useless at present to attempt to treat the possible small electronic displacements and polarities occurring within the ring.

Our consideration of electric moments has shown that alkyl groups do not differ sufficiently in electronegativity to cause any detectable electrical dissymmetry in saturated hydrocarbons. When a halogen atom is attached to a carbon chain, only the first two carbons are apparently affected electrostatically, the β-carbon but slightly. It may be supposed that the shifts of electron pairs induced by the strongly electronegative halogen, or, putting it in other terms, by the large doublet at the end of the chain, are too small, in the carbons beyond the first two, to have any measurable electrostatic effect. On the other hand, the ionization constants of the halogenated fatty acids in Table II show that the effect of a halogen is transmitted through five carbons and an oxygen. Moreover, the assumption of polarities arising from the different electronegativities of radicals appears to be useful in explaining and predicting chemical behavior. It is difficult to believe that polarities as small as they must be, if they exist at all, in the chains of the alkyl groups or in a symmetrically located double bond can have powerful directive influence or greatly affect chemical activity or degree of ionization. The moments of any doublets existing must be so small that they would exert considerable forces only at very short distances and, at these distances, the interatomic forces which vary inversely as a high power of the distance should be so large that one might

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[22] Williams, *Physik. Z.*, **29**, **683** **(1928).**

expect the effect of the forces due to the possible minute polarities to be negligible in comparison. In a molecule there is a possibility of a great variety of energy levels, many of which may differ from one another too little to give rise to measurable differences in polarity between molecules in which these levels are differently occupied. Too little is known of these levels in simple atoms to permit of intelligent reasoning in regard to complex compounds, but one cannot but wonder if the effects transmitted through long chains and the varied chemical behavior attributed to variation in polarity are not due to changes and differences in the energy levels occupied by the valence electrons. Polarity may occur, but ordinarily as an accompanying result rather than as a determining factor in chemical behavior. Although pronounced polarity is doubtless a factor in chemical behavior, a large portion of the polarities assigned by the various electronic theories of valence must be regarded not as a physical fact but merely as a pragmatic representation of chemical behavior.

Summary

Electric moments are used as a test of those electronic theories of valence which require polarity in the molecule. The absence of electric moment in methane, ethane and the higher paraffins shows that there is no measurable alternating polarity in the hydrocarbon chain or inherent dissymmetry in the electron linkages of alkyl radicals. The absence of variation in the moments of the higher ketones and alkyl halides leads to the same conclusion and shows that in these carbon chains no measurable polarity is transmitted through more than two atoms.

The ethylene double bond has no measurable polarity, but when different radicals are attached on opposite sides of the bond polarity may occur. The absence of rotation about the double bond is evidenced by the difference in moment between the cis and the *trans* isomers of the acetylene dihalides.

It is suggested that the directive influences and effects upon chemical activity commonly attributed to differences in polarity may be due rather to differences in the energy levels occupied by the valence electrons, which may or may not give rise to measurable polarity.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 216]

THE PREPARATION OF ANHYDROUS HYDROGEN IODIDE[1]

BY ROBERT T. DILLON[2] AND WILLIAM G. YOUNG[2]

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Introduction

In order to prepare chloroform solutions of anhydrous hydrogen iodide needed in the synthesis of 2-butene it was necessary to develop a process by which the desired gas could be obtained readily in large quantity.

Anhydrous hydrogen iodide has been prepared by the following methods: (a) passing hydrogen and iodine over platinum,[3] (b) heating iodine and colophony (resin),[4] (c) dropping water upon iodine and phosphorus, and (d) dropping hydriodic acid upon phosphorus pentoxide.[5]

For the purpose desired these methods have certain disadvantages, as follows: Method (a) is time-consuming and gives a product containing iodine unless a large excess of hydrogen is used or unless the product is liquefied and the hydrogen iodide distilled from the iodine; in Method (b) decomposition products of resin are likely contaminants of the hydrogen iodide; in Method (c) a considerable amount of phosphorus is reduced to phosphine, which is carried along in the gas stream, presumably in the form of phosphonium iodide, and explosions are liable to occur, especially at the beginning of the experiment; in Method (d), a small amount of phosphine is formed.

On the other hand, the different methods have certain advantages, as follows: by Method (a) hydrogen iodide of high purity may be prepared since both the hydrogen and iodine can without difficulty be freed of impurities, and by Methods (b), (c) and (d) a rapid evolution of hydrogen iodide may be obtained. Method (c) is the one usually employed for quantity production when a pure product is not needed, probably because the apparatus is comparatively simple, whereas Method (a) is used when a very pure product is desired. Method (b), apparently, is not generally recognized since it is mentioned only in standard reference works. It possesses obvious advantages as a rapid laboratory or lecture demonstra-

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[1] This paper contains results obtained in an investigation listed as Project No. 14 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] American Petroleum Institute Research Assistant, 1927–1928.

[3] Bodenstein, *Ber.*, **26,** 1146 (1893); *Z. phys. Chem.*, **13,** 56 (1894); Beckmann and Waentig, *Z. anorg. Chem.*, *67*, 17 (1910).

[4] Kastle and Bullock, *Am. Chem. J.*, *18*, 105 (1896).

[5] (a) A. van den Berghe, *Maandbl. Nat*, 22, 35 (1898); (b) Ruff, *Ber.*, 41, **3738** (1908).

tion preparation. This method was not considered by us because of the probable difficulties involved in removing the volatile decomposition products. Method (d) was tried out and an apparatus developed by the use of which pure anhydrous hydrogen iodide could be obtained rapidly in large quantities. This last is superior to Method (c) both as regards the purity of the product and the rate of production.

Apparatus and Method

Approximately 150 g. of concentrated hydriodic acid, sp. gr. 1.7, was placed in a dropping funnel, B (see figure) and was allowed to drop upon 200 g. of phosphorus pentoxide contained in a 0.5-l. conical flask, C, closed by a wired-on rubber stopper. A slight air pressure insured a steady flow of the acid into the generating flask. The evolved hydrogen iodide, containing traces of iodine, water and phosphine, was purified by passage through an all-glass apparatus. A glass tube, D, filled with phosphorus pentoxide removed mist produced by the vigorous reaction in the generating flask. Iodine and a part of the phosphonium iodide were taken out by a saturated solution of calcium iodide[6] at 0° contained in the bubbler, F. Water was absorbed by phosphorus pentoxide in the tube, G, and small amounts of phosphonium iodide were removed by passage through H, maintained at −25° to −30° by a cooling bath of ice and concentrated hydrochloric acid. The purified hydrogen iodide may be used as desired.

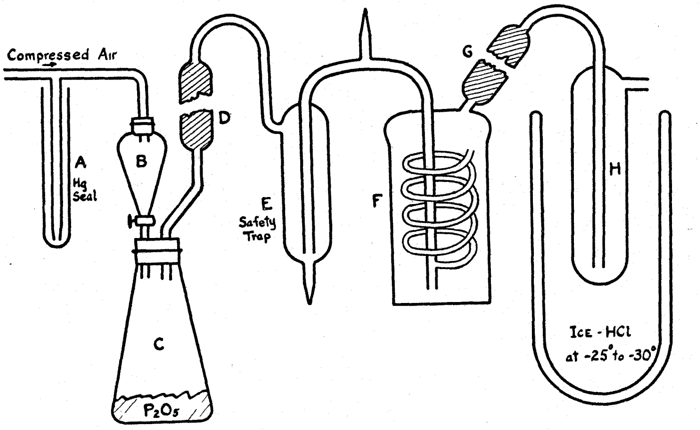

Fig. 1.

The calcium iodide solution, prepared by dissolving 200 g. of the salt in 100 g. of water, removed iodine completely. However, since anhydrous hydrogen iodide in the gaseous state and in solution, for example, in chloroform, is easily oxidized by air and rapidly decomposes when exposed to light, it was necessary to fill the apparatus with nitrogen for the first run and to protect it from light. This latter precaution is of vital importance for obtaining an iodine-free product because even weak, diffused daylight brings about decomposition. Between runs, in spite of these precautions, traces of iodine developed and for this reason it was necessary to discard the gas evolved at the beginning of each run. This formation of free iodine may have resulted in part from the presence of some air introduced while the phosphorus pentoxide supply was being replenished, even though the precaution was taken of passing a rapid stream of nitrogen through the flask before it was connected to the apparatus. Not more than 2 g. of phosphonium iodide crystallized out during the preparation of 650 g. of anhydrous hydrogen iodide. Its solubility in the calcium iodide solution is practically nil since the amount at the end of successive runs increased in proportion to the total hydrogen iodide produced. During each run there was formed in the generating flask a small amount of reddish powder, an intermediate reduction product of the phosphorus pentoxide, which was not investigated.

A saturated aqueous solution of hydrogen iodide prepared by this method gave a negative test for phosphate with ammonium molybdate.

The authors wish to express their appreciation to Professor Howard J. Lucas for his helpful suggestions in the work.

Summary

The description of a method and apparatus is given for the rapid formation of pure anhydrous hydrogen iodide. This is generated by dropping concentrated hydriodic acid upon phosphorus pentoxide and purified by bubbling through saturated calcium iodide, drying with phosphorus pentoxide and cooling to $-30°$.

PASADENA, CALIFORNIA

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

THE ELECTRONIC INTERPRETATION OF OXIDATION AND REDUCTION

BY WILLIAM ALBERT NOYES

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In several papers the attempt has been made to reconcile the positive–negative theory of valence, formerly advocated by myself, Stieglitz, Falk and Nelson, Fry, L. W. Jones and others,[1] with the theories of G. N. Lewis, Kossel and Langmuir, on the basis of the following principles.

1. Nearly all reactions occurring at ordinary temperatures are ionic in character.[2] For electrolytes this is identical with the positive–negative theory and is universally accepted. For other compounds this principle implies that the pair of electrons forming a covalence remains with one or the other of two atoms which separate as they prepare to enter into new combinations.[3]

2. There is a sharp difference between completely polar valences, in which one atom gains and the other loses an electron, and covalences, in which a pair of electrons is shared by two atoms. At the symposium of the Faraday Society in Cambridge, in 1923, I said "The difference

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[1] For references to the literature see THIS JOURNAL, 50, 2902 (1928).

[2] Noyes, *Chem. News*, 90, 228 (1904); THIS JOURNAL, 45, 2959 (1923).

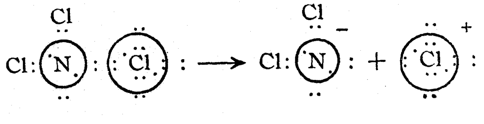
[3] For the hypothesis that a covalence consists of a pair of electrons rotating in opposite directions and including two nuclei within their orbits, see Robert Müller, "Der Aufbau der chemischen Verbindungen (Molekülbau)," Sammlung chem., chem.-tech. Vorträge, Bd. 30 (1928) and Noyes, *Proc. Nat. Acad. Sci.*, 13, 377 (1927).

between polar and non-polar valences is one of degree and not one of kind."[4] In making the statement I had in mind the ionization of weak acids and of tautomeric compounds and of carbon compounds which take part in condensations. It now seems to me better to make the distinction used here and to call covalences which more or less easily separate into positive and negative parts "potentially polar."[5] The distinction is chiefly one of nomenclature.

3. Covalences may be "potentially polar" for three reasons: (a) because one of the atoms has a larger kernel charge than the other and, therefore, a stronger attraction for the pair of electrons. The halogens, with a kernel charge of 7, nearly always retain the pair of electrons when they separate from a carbon atom, which has a kernel charge of 4. Hydrogen, with a nuclear charge of 1, leaves the pair with almost any atom from which it separates. There is no good evidence that it retains the pair and becomes a negative ion, except in separating from a metallic hydride.

(b) Because neighboring atoms in the molecule have a large kernel charge. The bromine of bromo-acetoacetic ester, $CH_3COCHBrCO_2C_2H_5$, is affected in such a manner that it leaves the pair of electrons with the carbon atom and separates in the positive form, $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}$, titrating with sodium thiosulfate as equivalent to two atoms of free bromine.[6] Hydrogen atoms attached to a carbon atom adjacent to a carboxyl or aldehyde group or to a carbon atom bearing an hydroxyl group, readily become hydrogen ions. This accounts for many condensation reactions and for the reactivity of alcohols in comparison with hydrocarbons.

(c) Because one of the atoms has a larger number of electrons in the kernel than the other and, for this reason, has less attraction for its valence electrons. The chlorine atoms of nitrogen trichloride give up their pairs of electrons to the nitrogen when the compound is decomposed by hydrochloric acid,[7] in spite of the kernel charge of 5 on the nitrogen atom and of 7 on the chlorine atom, because there are only *2* electrons in the kernel of the nitrogen atom and 10 in the kernel of the chlorine



Phosphorus trichloride, on the other hand, hydrolyzes to phosphorous acid and hydrochloric acid because there are 10 electrons in the kernels

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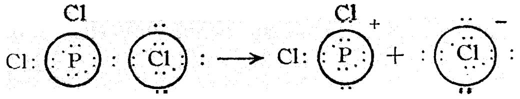
[4] Noyes, *Trans. Faraday Soc.*, 19, *476,* 478 (1923).

[5] Noyes, *Z. physik. Chem.*, 130, *325,* 329 (1927).

[6] Kurt *Meyer, Ann., 380,* 217 (1911); Noyes, *"Organic Chemistry," Henry* Holt **and *Co.*,** 1926, p. 420.

[7] Noyes, THIS *JOURNAL,* 42, 2173 (1920).

of both phosphorus and chlorine, while the kernel charge of phosphorus is 5 and that of chlorine is 7:



4. In compounds containing only covalences, the number of covalences plus the number of unshared electrons is equal to the number of valence electrons for each atom.

5. In ions, whether simple or complex, there is always some atom which has completed its octet by uniting with a larger or smaller number of electrons than is called for by 4.

6. Atoms may be doubly united either by a doubled covalence or by one covalence and one polar union.

Adherents of the positive–negative theory in its earlier form defined oxidation as the loss and reduction as the gain of electrons. A consideration of the electronic mechanisms in the light of the principles given, leads us to distinguish three types of oxidation.

1. Transfer of an Electron.—When sodium is oxidized by chlorine, the electrons of two sodium atoms are transferred to a molecule of chlorine, giving two chloride ions. When sodium reacts with water, each sodium atom gives its electron to a hydrogen ion, which is the real oxidizing agent. The hydrogen ions are reduced to free hydrogen.

When aluminum dissolves in a solution of sodium hydroxide, there is a similar exchange of electrons between the aluminum and the hydrogen ions of the solution, though the latter are present in small numbers. The fact that the hydroxyl ions unite with the aluminum with a covalence, giving an amphoteric hydroxide and reducing the hydroxyl-ion concentration, is probably an important factor in the phenomenon.

The oxidation of *o*- or *p*-cresol, with evolution of hydrogen,[8] when they are fused with potassium hydroxide, is best explained in a similar manner. The semipolar oxygen atom of the cresylate ion, $CH_3C_6H_4{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{:}^-$, enhances the tendency of the hydrogen atoms of the methyl group in the ortho or para position to assume the ionic form, as the hydrogen atoms in the ortho and para positions do in the Kolbe and Reimer–Tiemann syntheses. The hydrogen ions, in this case, do not escape as positive ions, however, but take the electrons from the carbon atom of the methyl group and unite with hydrogen ions of the water, forming free hydrogen. This is essentially the explanation given by Professor Fry, for a similar reaction, at the Columbus symposium.

2. Oxidation by Positive **Hydroxyl.**—This explanation has been given[9]

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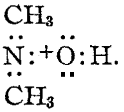
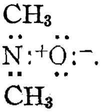
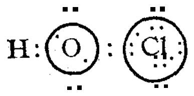
[8] Barth, *Ann*, **154, 359** (1870).

[9] Noyes, Bull. *soc. chim.*, 35,437 (1924).

for the oxidation of trimethylamine to trimethylamine oxide by hydrogen peroxide. Hydrogen peroxide separates into a positive hydroxyl, $H:\overset{\cdot\cdot}{O}{}^{+}$, and a negative hydroxyl, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}H$, in the same way that a molecule of chlorine separates into positive chlorine, $:\overset{\cdot\cdot}{Cl}{}^{+}$, and negative chlorine, $:\overset{\cdot\cdot}{Cl}:^{-}$, in reacting with water. This positive hydroxyl can add itself to the two free electrons of the trimethylamine, oxidizing the electrically neutral nitrogen atom to the ionic form,  $CH_3:\overset{CH_3}{\underset{CH_3}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}}}:{}^{+}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H$. If hydroxyl ions, which have a strong affinity for hydrogen ions, are present, the hydrogen will unite with these, leaving a semipolar union between the oxygen and the nitrogen,  $CH_3:\overset{CH_3}{\underset{CH_3}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}}}:{}^{+}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$. If a chloride or bromide ion is present, this does not happen.[10]

The intermolecular oxidation of three moles of hypochlorous acid to chloric acid and hydrochloric acid is most easily explained by a consideration of the close balance in the attraction of the oxygen and chlorine atoms for the pair of electrons forming the covalence between them:



. The chlorine atom with a kernel charge of 7, and 10 electrons in its kernel, has almost the same attraction for the pair of covalence electrons as the oxygen atom has, with a kernel charge of 6 and only two electrons in its kernel.

It has been shown[11] that hypochlorous acid gives the four ions H^{+}, ClO^{-}, HO^{-} and Cl^{+}. Because of the balance between the oxygen and chlorine, two other ions are probable; a positive hydroxyl ion, $H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}{}^{+}$, and the negative chloride ion, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:^{-}$. By the union of the positive hydroxyl with a mole of hypochlorous acid, the compound $H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{}^{+}:\underset{\cdot\cdot}{O}:H$ is formed. The chlorine atom of this compound is positive because the sum of the covalences and unshared electrons is only 6. The loss of a hydrogen atom as an ion leaves a semipolar union between the chlorine and oxygen, $H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{}^{+}:\underset{\cdot\cdot}{O}:^{-}$. The hydrogen ion, on the other hand, balances the chloride ion left when the hypochlorous acid separates into positive hydroxyl and negative chlorine. A repetition of this process gives chloric acid.

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[10] Noyes, THIS JOURNAL, 47, 3025 (1925).

[11] Noyes and Wilson, *ibid.*, 44, 1630 (1922).

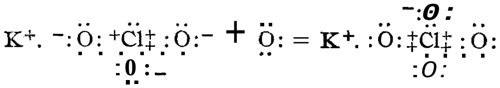
Because of the accumulation of semipolar oxygen atoms, chloric acid has a high ionization constant while that of hypochlorous acid is very small.

F. Foerster[12] nearly thirty years ago gave the following ionic interpretation for the formation of chloric acid

$$ClO^- + 2HOCl = ClO_3^- + 2H^+ + 2Cl^-$$

It will be seen that this is equivalent to the electronic interpretation here given, but less detailed.

3. Oxidation by Semipolar Oxygen Atoms.—When potassium chlorate is kept at its melting point, in the absence of a catalyst, it may be largely converted to potassium perchlorate. This may be explained by supposing the transfer of an electrically neutral oxygen atom from one mole of the potassium chlorate to another



$$K^+.\ ^-{:}\ddot{O}{:}\underset{:\ddot{O}:^-}{{}^+\ddot{Cl}{\ddagger}}{:}\ddot{O}{:}^- + \ddot{O}{:} = K^+.\ {:}\ddot{O}{:}\overset{^-:O:}{\underset{:O:}{{\ddagger}\ddot{Cl}{\ddagger}}}{:}\ddot{O}{:}$$

The oxidation of alcohols by nitric acid, potassium permanganate and other agents which contain semipolar oxygen atoms is probably of this type.

The presence of oxygen in a carbon compound enhances the tendency of the hydrogen atoms attached to the same or to an adjacent carbon atom to separate as positive hydrogen ions. It is well known, of course, that the hydrogen of a primary or secondary alcohol or of an aldehyde group is easily replaced by hydroxyl. In the simplest case, methyl alcohol separates into $H{:}\underset{H}{C}{:}{}^-O{:}H$ and H^+. An electrically neutral oxygen atom would engage the pair of electrons of the carbon atom, but the added oxygen atom would now be negative, $H{:}\overset{:\ddot{O}:^-}{\underset{H}{C}}{:}O{:}H$ and would take up the hydrogen ion. In the compound which results, $H{:}\overset{:\ddot{O}:H}{\underset{H}{C}}{:}O{:}H$, the balance of the affinity of the carbon for the hydroxyl and of the oxygen for the hydrogen, which causes these to separate as water, leaving a double union between the carbon and the oxygen, is well known. That the carbon is doubly united with the oxygen in aldehydes, ketones and acids has been shown by Sugden.[13]

Theoretically any semipolar oxygen atom may separate with its six

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[12] F. Foerster, *J. prakt. Chem.*, [2] 63, 147 (1901).

[13] Sugden, *J. Chem. Soc.*, 125, 1183 (1924); 127, 1525, 1580 (1925).

valence electrons without disturbing the electronic balance of the atom from which it separates.

Summary

There seem to be at least three types of oxidation reactions.

1. Oxidation by the transfer of an electron from one atom to another.
2. Addition of a positive hydroxyl group, $H:\ddot{O}+$, to an unshared pair of electrons, either of a negative ion or of an electrically neutral molecule. In the latter case a hydrogen ion separates and a semipolar union is formed.
3. Separation of a semipolar oxygen atom in an electrically neutral condition followed by its union with an unshared pair of electrons. The oxygen atom may either remain in the semipolar condition in the new compound or may take up a hydrogen ion and form an hydroxyl group.

URBANA, ILLINOIS

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

TERNARY SYSTEMS. VIII. POTASSIUM CARBONATE, POTASSIUM SULFATE AND WATER AT 25°

BY ARTHUR E. HILL AND SAMUEL MOSKOWITZ

RECEIVED APRIL 15, 1929 PUBLISHED AUGUST 7, 1929

The solubilities of potassium carbonate and potassium sulfate in water have been studied by Blasdale* and more recently by de Ropp,[2] in both cases as part of a study of a four-component system. The two papers give data for the solubilities, however, at the isothermally invariant points only; the solubilities at intermediate concentrations having been determined in this Laboratory, the results are communicated to complete the picture.

Anhydrous potassium carbonate (Kahlbaum's "zur Analyse") and potassium sulfate (purified by recrystallization) were taken in weighed amounts and agitated with measured amounts of water at 25 ± 0.05" until equilibrium was attained, three days being found to be a sufficient time. The saturated solution was analyzed for carbonate by titration against acid, using methyl orange as indicator, with correction for the effect of the sulfate on the end-point. Water was determined as loss by evaporation from platinum dishes. Sulfate was determined only when the amounts had become small, in Line 6 by precipitation as barium sulfate from an acid solution, and in Lines 7, 8 and 9 turbidimetrically. Direct weighing of small pipetted samples gave values for the density of the solution.

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[1] Blasdale, THIS JOURNAL, 45, 2935 (1923).

[2] Teeple, "Industrial Development of Searles Lake Brines," Chemical Catalog Company, New York, 1929, p. 72.

TABLE I

SYSTEM K_2SO_4–K_2CO_3 H_2O AT 25°

No.	Original complex K_2SO_4, wt %	Original complex K_2CO_3, wt. %	Saturated solution K_2SO_4, wt. %	Saturated solution K_2CO_3, wt. %	Density	Solid phase
1	..	..	10.7	..	1.083	K_2SO_4
2	21.8	4.6	6.5	6.5	1.103	K_2SO_4
3	17.2	8.3	4.9	8.4	1.122	K_2SO_4
4	17.1	14.1	2.8	16.4	1.170	K_2SO_4
5	13.7	20.4	1.5	23.2	1.230	K_2SO_4
6	14.6	30.1	0.3	35.0	1.348	K_2SO_4
7	8.1	41.5	.08	45.1	1.465	K_2SO_4
8	16.6	40.6	.03	48.6	1.506	
9	8.4	51.6	.03	52.8	1.557	K_2SO_4 +
	2.1	54.8				$K_2CO_3 \cdot 3/2H_2O$
10	..	..	..	52.8	1.557	$K_2CO_3 \cdot 3/2H_2O$

It appears from the table, and also from the figure, that the solubility of the potassium sulfate is reduced to less than 0.1% when the solution is still far from saturation with respect to carbonate, and to 0.03% at the saturation point. It is striking that the solubility is so greatly lessened by the presence of potassium carbonate; so great a salting-out effect upon a reasonably soluble salt is not common.

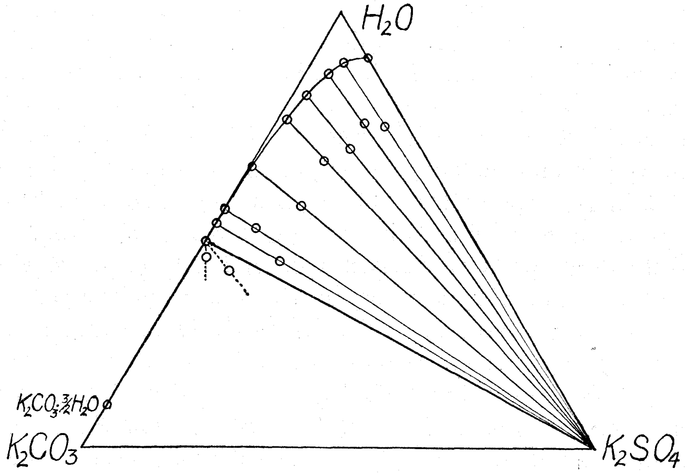

Fig. 1.—25° Isotherms for K_2CO_3–K_2SO_4–H_2O.

Especial attention was paid to the question of possible solid solution of the two salts, since the corresponding sodium salts form the well-known solid solution Glaserite. Algebraic extrapolations of the tie lines from saturated solution through original complex all fell somewhat short of the point representing 100% K_2SO_4, by a matter of several tenths of 1% up to over 1%. Two crystallization experiments, however, from solution rich in carbonate gave solids which analyzed at 99.89 and 99.91% of K_2SO_4, respectively, after correction for the small amount of adhering solution; from this we conclude that the direction of the tie lines was influenced by a small systematic error in the analytical work and that solid solution does not occur in the system at 25° to a measurable extent.

Summary

The solubility of potassium carbonate and potassium sulfate in the ternary system with water at 25° has been measured. Solid solution has not been found to occur.

NEW YORK CITY

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

A GENERAL METHOD OF MEASURING THE PARTIAL PRESSURE OF MERCURY AT ROOM TEMPERATURES

BY L. L. HIRST AND A. R. OLSON

RECEIVED APRIL 15, 1929 PUBLISHED AUGUST 7, 1929

Two methods of determining the activities of amalgam constituents have been used. In the first of these methods the calculation is based on measurements of the electromotive forces of concentration cells. This method has been used successfully in investigating a number of amalgams. In some cases, however, a serious difficulty is encountered. Thus with cesium and barium amalgams, no liquid is known which dissolves enough of the salt to make the liquid sufficiently conducting, and which at the same time is unreactive enough so that no side reactions occur with the metal. In the second method, vapor pressures of amalgams have been measured at high temperatures. The data so obtained must be extrapolated to 25° in order to be used in connection with other data. Because of these difficulties, we have devised a general method of obtaining the partial pressures of mercury over any amalgam at room temperatures.

When light from a mercury arc under properly controlled conditions falls on mercury vapor, the resonance line 2536 Å. is absorbed according to the equation $I = I_0e^{-\alpha pd}$, in which I is the intensity of the transmitted light, I_0 is the intensity of the incident light and a, p and d are the absorption coefficient, the pressure of mercury and the thickness of the absorbing gas layer. If a were a constant, we could determine p directly by measuring the quantity I/I_0. However, it has been shown by Hughes and Thomas[1] that a is not a constant even when a mercury resonance lamp is substituted for the mercury arc. a is also affected by the pressure of foreign gas even though these gases themselves have a negligible absorption for this line. Fortunately it was possible to determine p without evaluating a.

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[1] Hughes and Thomas, *Phys. Rev.*, **30**, 466 (1927).

In the work of Olson and Meyers[2] it was shown that if mercury resonance radiation falls on a mixture of hydrogen, ethylene and mercury vapor, a reaction occurs which results in a pressure decrease. It was further shown that this reaction was sensitive only to the resonance line (somewhat broadened due to the presence of gases). This reaction, therefore, can be used to measure the amount of mercury resonance light falling on it in a given time.

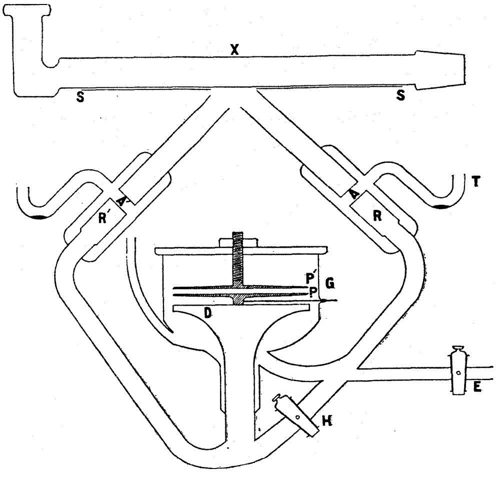

Fig. 1.

The experimental arrangement of our apparatus is shown in Fig. 1. Light from the mercury arc X was passed through the absorption cells A,A' and then into the reaction chambers R,R'. The shield S was used to limit the region of the arc from which light could come. The arc was water cooled and subjected to a magnetic field in the usual way. The absorption chambers were connected to side tubes TT' in which mercury or amalgam could be placed and kept at any desired temperature, and also to the vacuum line so that they could be evacuated or specific gases at known pressures admitted. The reaction chambers were connected to the vacuum line through the stopcocks H and E. They were also connected to the two sides of the differential pressure gage which we have already described.[3] During these experiments the above apparatus with the exception of the arc and the side tube T' was kept in a water thermostat at a temperature of **26.0 ± 0.02"**.

The reaction chambers were filled with a mixture of **93** mole % of hydrogen and 7 mole % of ethylene and saturated with mercury vapor. Stopcocks H and E were then closed. Pure mercury was placed in the side tubes TT' together with **10** cm. of hydrogen. The temperature of the mercury in T' varied from liquid air temperatures to the thermostat temperature. Light from the arc was then permitted to pass through the absorption cell **A,** and the time required to produce a given pressure change in R was noted. The light was next passed through **A'** for a long enough time to produce the same pressure change in R'. This was repeated a number of times and the average rate for each side was calculated. The average rate was necessary in order to minimize the error due to fluctuations in the arc. The change of composition of the reacting mixture was small, for the gage was sensitive to small pressure changes. Even if it had been large, it would have introduced no error for the change was the same in both R and R'. The temperature of T' was then changed, and the above process repeated. The rate of reaction in R decreased with time due to a gradual blackening of the lamp walls, and so the average rates in R' were corrected by the factors necessary to make the rates in R constant. The following table will serve to show how the experimental data were treated,

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[2] Olson and Meyers, THIS JOURNAL, 48, **389 (1926).**

Olson and Hit, *ibid.*, 51, **2378** (1929).

TABLE I

TREATMENT OF EXPERIMENTAL DATA

R at 26°, rate div./min.	10	9	9.7	9.6	9.8	9.0	9.0	8.6	9.4
R' at 0°, rate div./min.	26.0	24.0	26.5	26.0	25.5	24.5	25.5	26.5	26.0
R at 26°, rate div./min.	8.9	9.0	8.6	8.2	9.2	9.8	Av.	9.2	
R' at 0°, rate div./min.	250	24.5	25.0	25.0	25.5	..	Av.	25.4	

Standard rate for R = 12.3. Therefore corrected rate for R' = (12.3/9.2) X 25.4 = 34.0.

Table II lists all of the corrected average rates.

TABLE II

CORRECTED AVERAGE RATES

Temp., °C.	88	273.1	277.9	282.8	287.0	291.1	299.1
Av. rate div./min.	43.0	34.0	31.3	27.0	21.6	16.9	12.3
Press. Hg, cm. X 10^5	0	1.98	3.20	4.92	7.36	10.72	20.1

The vapor pressures of mercury in the last line of Table II were calculated by the equation of Randall and Langford[4] for the free energy of mercury. In Fig. 2 we have plotted the average rate against the mercury pressure in the absorption cell A'.

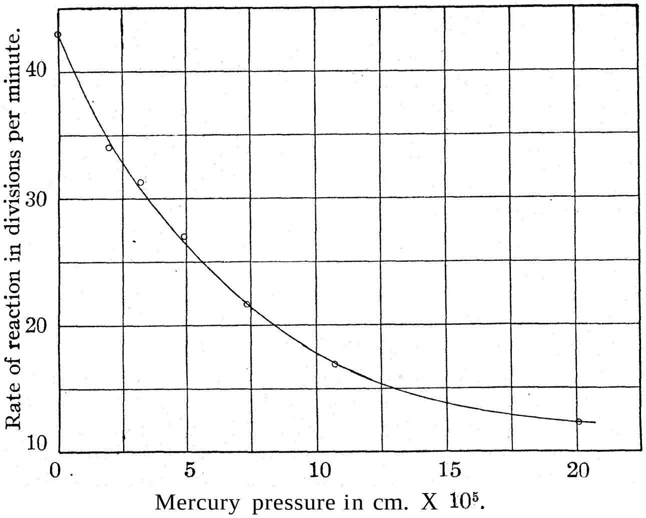

Fig. 2.

Thallium amalgams were then substituted for pure mercury in T', and kept at the temperature of the thermostat. The rate of change of pressure with time was determined as before. The amalgams were analyzed by the method of Richards and Daniels.[5] The pressure of mercury corresponding to each rate was then obtained from the curve in Fig. 2. From

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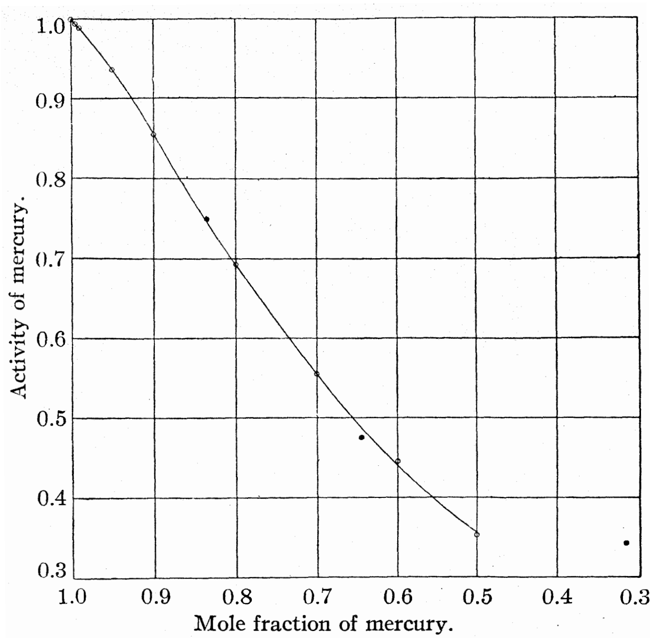
[4] Randall and Langford, unpublished work.

[5] Richards and Daniels, THIS JOURNAL, 41, 1731 (1919).

these pressures and the pressure of pure mercury at 26°, the activities of the mercury in the amalgams were calculated. Table III summarizes these measurements and calculations. The activity of mercury is plotted in Fig. **3,** together with the activity calculated from the electromotive force



○, Richards and Daniels; ●, Hirst and Olson.

Fig. 3.

measurements of Richards and Daniels.[6] It is to be noted that the most concentrated amalgam is a solid.

TABLE III

VAPOR PRESSURE AND ACTIVITIES OF THALLIUM AMALGAMS AT 26°

N_1	1.000	0.835	0.644	0.316
Av. rate	12.3	13.6	18.3	22 5
Press. Hg, cm. × 10^5	20.1	15.15	9.6	6.9
Activity	1.000	0.755	0.477	0.344

It was mentioned above that hydrogen was admitted to the absorption cells. This was necessary in order to make the breadth of the absorption line of mercury about equal to that of the mercury in the reaction chambers. The pressure of hydrogen necessary to do this was determined by measuring the reaction rates for a given pressure of mercury and variable pressures of hydrogen in the absorption cell. Figure 4 shows the depen-

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[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 270.

dence of the rate on the hydrogen pressure. A slow rate corresponds to a large absorption in the cell. This is the condition for high sensitivity with respect to mercury pressure in the absorption cell. The curve is practically horizontal at 10-cm. pressure; a further increase of hydrogen pressure would slow up the establishment of equilibrium and a decrease would make the method less sensitive to changes in mercury pressure.

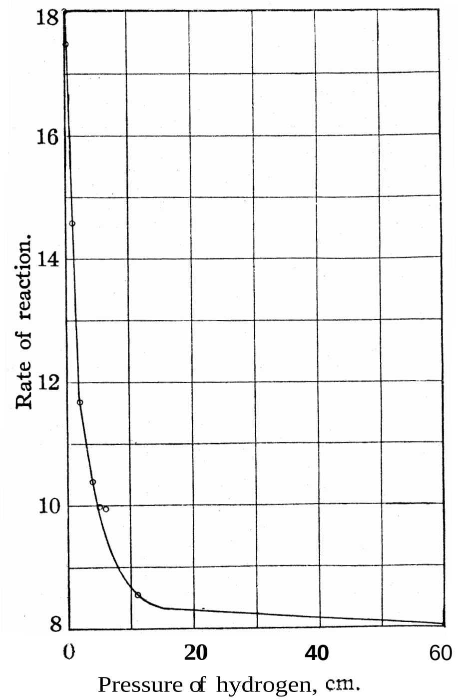

Fig. 4.

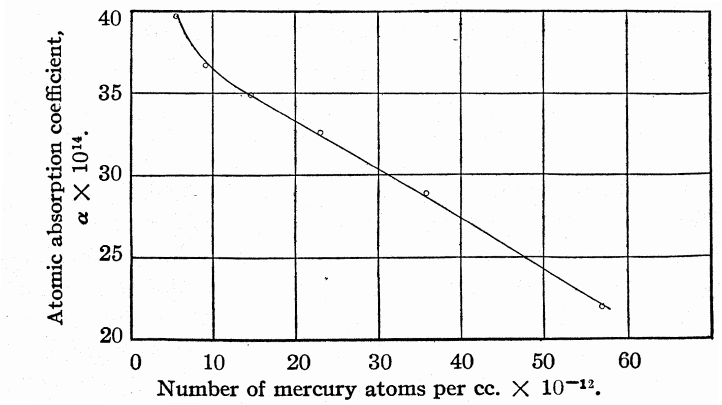

Fig. 5.

From the known pressures and rates as plotted in Fig. 2, it is possible to calculate an average atomic absorption coefficient form ercury at various pressures when subjected to a pressure of 10 cm. of hydrogen. This calculation has been made and the results are plotted in Fig. 5. The absorption coefficient shows the same type of variation that was noted by Hughes and Thomas[1] for pure mercury under its own vapor pressure.

Conclusion

The vapor pressures of mercury over thallium amalgams at 26° have been determined. From these the activities have been calculated and shown to agree reasonably well with those calculated from the electromotive force measurements of Richards and Daniels. The broadening of the absorption line of mercury by hydrogen for its own resonance light has been studied, and the change in the atomic absorption coefficient of mercury in the presence of hydrogen for its resonance line has been determined.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO METHYL TIN DERIVATIVES. I. INTRODUCTION. II. ACTION OF ZINC ON TRIMETHYL TIN BROMIDE. III. TRIMETHYL TIN PHENOLATE. IV. DECAMETHYLSTANNOBUTANE

BY CHARLES A. KRAUS AND ARTHUR M. NEAL

RECEIVED APRIL 18, 1929 PUBLISHED AUGUST 7, 1929

I. Introduction

The heavier elements of the fourth group are, in many respects, analogous to carbon. Various hydrides of these elements have been prepared and their properties have been found to correspond fairly closely with those of corresponding carbon compounds. The stability of the hydrides decreases with increasing atomic number, so that their study is not generally practicable. We have but few radicals of these elements corresponding to methyl, ethyl, phenyl, etc.

However, if the hydrogen atoms attached to an element, such as tin, are substituted by alkyl or aryl groups, radicals are obtained whose properties correspond closely to those of similar carbon radicals. Thus the group $(C_6H_5)_3Sn$, or triphenylstannyl, bears a close physical and chemical resemblance to triphenylmethyl, $(C_6H_5)_3C$. In the case of most carbon compounds, the tendency of two unsaturated carbon atoms to combine with each other is so great that stable coupling occurs and the group becomes inactive. On the other hand, in the case of the corresponding tin compounds, the coupling is relatively weak and the groups exhibit marked reactivity.

while-such compounds as sodium methyl, sodium ethyl, etc., have been obtained, their reactivity is so great that they are not generally usable for synthetic purposes. This difficulty, in the case of carbon compounds, has been largely overcome through the use of the Grignard reagent, in which an alkyl or aryl group is coupled to magnesium. In the case of tin, compounds of the type $NaSnR_3$ or Na_2SnR_2 are readily obtained and they are convenient reagents for introducing the organic tin groups into various compounds. The alkali metal salts mentioned serve very much the same purpose in the chemistry of tin that the Grignard reagent does in the chemistry of carbon.

Compounds such as sodium trimethyl tin, $NaSnR_3$, are readily soluble in liquid ammonia and in this solvent they react conveniently with many other substances, particularly halogenated compounds. Kraus and Greer[1] have described a number of syntheses in which sodium trimethyl tin was used. In the present investigation the use of the same reagent has been extended to the preparation of various compounds. A considerable number of incidental problems developed which it was found necessary to study and an account of these will be given in the sequel.

II. Action of Zinc on Trimethyl Tin Bromide

Frankland[2] reported that triethyl tin is formed by the action of zinc on triethyl tin chloride in aqueous solution. With a view to utilizing a similar reaction in the preparation of trimethyl tin, the action of zinc on trimethyl tin bromide was investigated. It was found that while reaction takes place between trimethyl tin bromide and zinc, no trimethyl tin is formed. Instead, there are produced tetramethyl tin, trimethyl tin hydroxide and metallic tin.

Procedure.—Trimethyl tin bromide was prepared by adding an equivalent quantity of bromine to tetramethyl tin in the cold,[3] the product being purified by fractional distillation. About 40 grams of this bromide, dissolved in 100 cc. of water, was sealed in a tube with freshly polished strips of zinc. The tube was fitted with a stopcock through which it was evacuated. It was then placed in a bath of boiling water for several days. Initially a red solid was precipitated on the surface of the zinc, but on continued

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[1] Kraus and Greer, THIS JOURNAL, 47, **2568 (1925).**

[2] Frankland, **Ann.** *Chem. Pharm.,* **85,329 (1853).**

[3] This method of preparing the various halogenated derivatives of tetramethyl tin has since been abandoned in this Laboratory. Mr. Stafford has shown that by heating mixtures of tetramethyl tin with stannic chloride in appropriate proportions, the monochloride, dichloride or trichloride may be obtained at will in practically pure condition. The two liquids are mixed in the cold and the mixture is later heated in a sealed tube until the reaction is complete. The same method has been employed by Mr. Eatough in preparing halogenated derivatives of tetraphenyl tin. This method of preparation is advantageous since there is no loss of organic groups and substantially pure products are obtained. Since writing the above, the same method has been described by K. *A.* Kozeschkow, *Ber.,* 62, **996 (1929).**

heating this disappeared and a volatile yellow oil appeared and settled in the bottom of the tube.

After separating the oil from the supernatant liquid by means of a separatory funnel, it was fractionally distilled. Toward the end of this process needle-like crystals appeared and similar crystals also appeared in the original tube on standing. These crystals volatilized readily, when gently heated, indicating that they were trimethyl tin hydroxide.

The Products of Reaction.—The vapor density of the purified oil was determined and its molecular weight calculated. Using a bulb having a volume of 256 cc., the following data were obtained: 0.1945, 0.1575, 0.2031 g. of subs. at 78.5, 64.2, 81.2-mm. pressure and 26.9, 29.0, 27.2° correspond to the mean molecular weights 181.0, 180.4, 182.6; mol. wt. of $(CH_3)_4Sn$, 178.8.

The boiling point of the liquid was found to be 77.5° (uncorr.); the boiling point of tetramethyl tin is 78.0°. The vapor pressure of the liquid corresponded closely with that of tetramethyl tin. Thus at 0 and 27.7°, the vapor pressure of the liquid was found to be 3.5 and 12.0 mm., respectively, as against 3.6 and 11.6 for tetramethyl tin at the same temperatures.

The strips of zinc were removed from the reaction tube and carefully washed. They were found to be covered with a metallic coating, which was scraped off, dissolved in hydrochloric acid and tested with hydrogen sulfide. A yellow precipitate was formed, indicating the presence of tin.

The action of zinc on trimethyl tin bromide differs from that on triethyl tin bromide. While in the latter case triethyl tin is formed, in the former a complex reaction occurs, the chief product being tetramethyl tin. At the same time, trimethyl tin hydroxide and metallic tin are formed in appreciable quantity.

III. Trimethyl Stannyl Phenolate, $C_6H_5OSn(CH_3)_3$

Preparation.—The phenolate of trimethyl tin is readily prepared by the action of trimethyl tin bromide on sodium phenolate in liquid ammonia. Reaction occurs according to the equation

$$C_6H_5ONa + (CH_3)_3SnBr = C_6H_5OSn(CH_3)_3 + NaBr$$

Sodium phenolate is best prepared by adding phenol, in small portions, to a solution of sodium in liquid ammonia. On adding trimethyl tin bromide to the resulting solution of sodium phenolate, trimethyl tin phenolate is immediately precipitated. The product of the reaction was extracted with ether and, after distilling off the excess solvent, the phenolate was distilled under a pressure of 8 mm. at 109°. Under normal pressure, the liquid boils at 223–224° with some decomposition. It is stable in air in the pure condition but becomes colored on exposure to sunlight. It remains liquid at the temperature of boiling ammonia.

Analysis.—The tin content of the compound was determined by the Carius method. Subs., 0.4015, 0.5213: SnO_2, 0.2381, 0.3111. Calcd. for $C_6H_5OSn(CH_3)_3$: Sn, 46.2. Found: Sn, 46.68, 47.00.

Molecular Weight.—The molecular weight was determined by the freezing point method in benzene in the usual manner. Solvent, 37.03, 37.03 g.; solute, 1.389, 1.927; Δt, 0.718, 1.476°; mol. wt. found, 261.1, 267.7; mol. wt. calcd. for $C_6H_5OSn(CH_3)_3$, 257.

Characterization.—When trimethyl tin phenolate is treated with two equivalents of sodium in liquid ammonia, the following reaction occurs

$$(CH_3)_3SnOC_6H_5 + 2Na = NaSn(CH_3)_3 + C_6H_5ONa$$

The resulting solution is colored slightly yellow due to the sodium trimethyl tin. On adding ethyl bromide to the solution, phenetole and ethyl trimethyl tin are formed. The odor characteristic of phenetole was noticeable but it was not found possible to separate it from the associated tin compound. Accordingly, a solution of trimethyl tin phenolate was treated with one atom of sodium, in which case reaction proceeds as follows

$$2(CH_3)_3SnOC_6H_5 + 2Na = [(CH_3)_3Sn]_2 + 2NaOC_6H_5$$

The precipitated trimethyl tin was allowed to settle, the supernatant liquid was siphoned off and the trimethyl tin was repeatedly washed with fresh ammonia. The insoluble product left behind in the reaction tube melted at 23–25°, which agrees with the melting point of trimethyl tin. On brominating this material, trimethyl tin bromide was identified.

The washings containing sodium phenolate were neutralized with acid and treated with bromine water. A heavy white precipitate was formed, which is characteristic of phenol. On extracting an aqueous solution of the hydrolyzed product with ether and removing excess solvent, an oily liquid was obtained having the odor of phenol.

IV. Decamethylstannobutane

Kraus and Greer have prepared methylated tin derivatives containing chains of three and five tin atoms, corresponding to the general formula $(CH_3)_n + {}_2Sn_n$. In order to complete this series, the corresponding butane was synthesized.

Preparation.—The method of Kraus and Greer was employed, disodium tetramethylstanno-ethane being first prepared by treating two moles of dimethyl tin dibromide with six moles of sodium. Reaction takes place according to the equation

$$2(CH_3)_2SnBr_2 + 6Na = 4NaBr + Na(CH_3)_2Sn{-}Sn(CH_3)_2Na$$

The butane was then prepared by treating the ammonia solution of the above stannide with two moles of trimethyl tin bromide. Reaction proceeds according to the equation

$$Na(CH_3)_2Sn{-}Sn(CH_3)_2Na + 2(CH_3)_3SnBr = \\ (CH_3)_3Sn{-}Sn(CH_3)_2{-}Sn(CH_3)_2{-}Sn(CH_3)_3 + 2NaBr$$

Reaction takes place readily with separation of the stannobutane in liquid form. After evaporation of the ammonia, the liquid was dissolved in ether, the resulting solution was filtered and the ether removed with a pump.

Analysis.—The final product of reaction was analyzed for tin by the Carius method. Subs., 0.2443, 0.1110: SnO_2, 0.2357, 0.1066. Calcd. for $(CH_3)_{10}Sn_4$: Sn, 75.96. Found: Sn, 76.00, 75.65.

Molecular Weight.—The molecular weight of the compound was determined in benzene by the freezing point method. Solvent, 21 90, 21.90 g.; solute, 0.7371, 0.1098 g.; *At*, 0.276, 0.040°; mol. wt. found, 610,627; mol. wt. calcd. for $(CH_3)_{10}Sn_4$, 625.

Properties.—The pure compound is a colorless liquid which is somewhat viscous. It oxidizes readily with the formation of a white solid.

With this compound, the complete series of derivatives up to and including the pentane have been synthesized. The synthesis of the butane further confirms the mechanism of the reduction reactions of the dimethyl tin halides suggested by Kraus and Greer.[4]

Summary

1. The action of zinc on trimethyl tin bromide in aqueous solution has been studied. The chief product of reduction is tetramethyl tin. Some trimethyl tin hydroxide and metallic tin are alsa formed.

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[4] Kraus and Greer, THIS JOURNAL, 47,2570 (1925).

2. Trimethylstannyl phenolate, $C_6H_5OSn(CH_3)_3$, has been prepared by the action of trimethyl tin bromide on sodium phenolate.

3. Decamethylstannobutane, $(CH_3)_{10}Sn_4$, has been prepared.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES.

II. IMPROVEMENTS IN THE OSCILLATOR AND DETECTOR

BY GRINNELL JONES AND GILES M BOLLINGER

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The new form of alternating current bridge described in the first paper of this series[1] has been used in the study of the principles of design of cells for the measurement of the conductance of solutions. Although in most respects this bridge has met our most exacting requirements, a few improvements in the accessories of the bridge have been made which it seems desirable to describe without waiting until the results on cell design can be published.

Modification of the Oscillator to Give Low Voltages.—During the work on cells it became evident that it would be advantageous to reduce the voltage used considerably below the values (2 to 5 volts) which had been used in the study of the bridge itself and in the study of resistance boxes, in order to reduce the heating effect of the current on the cells and to study polarization and the variation of resistance with voltage which has been reported by others.[2]

The vacuum tube oscillator as originally built and described in the first paper of this series contained an output coil having 140 turns and when this coil was as close as possible to the oscillating coil, gave a maximum voltage of 5.2 volts at 2280 cycles, 4.3 volts at 1090 cycles and 2.3 volts at 500 cycles, when used to measure 10,000 ohms in the bridge. When measuring lower resistances, the voltage was somewhat less. The voltage could be diminished continuously down to about 0.2 volt by moving the output coil along its axis away from the oscillating coil to a distance of six inches, thus diminishing the inductive coupling. To reduce the voltage still more by moving the coil still farther away from the controlling coil did not seem to be wise because this would reduce the influence of the controlling coil without at the same time reducing the influence of outside disturbing factors such as electric light circuits and nearby electric motors. An attempt to reduce the voltage by the use of

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[1] Grinnell Jones and R. C. Josephs, THIS JOURNAL, 50, 1049 (1928).

[2] W. A. Taylor and S. F. Acree, ibid., 38, 2416 (1916); C. A. Kraus and H. C. Parker, ibid., 44, 2438 (1922).

taps on the output coil proved to be unsatisfactory and was abandoned. When a tap is used, the unused turns in the coil are thus appended in an unsymmetrical manner to one end of the effective part of the output coil. The unbalanced capacitance between this appended portion and the grounded shield makes it difficult to make a proper ground balance. We, therefore, built two additional output coils, one of 36 turns and one of 12 turns, each shielded by a grounded toroidal coil as described in the first paper, and mounted so as to be movable on their common axis, making it possible to vary the closeness of the coupling with the oscillating coil. The coils not in use are completely disconnected from the circuit. As thus modified our oscillator can be adjusted so as to give any desired voltage from the maximum stated above down to 0.01 volt. Above 0.3 volt these voltages can be measured by means of a thermal voltmeter. Below 0.3 volt the voltages can be estimated with sufficient accuracy for our purposes from the position of the output coil with reference to the oscillating coil. Additional condensers of smaller capacitance than those originally provided were added to the oscillator so that by their use the frequency could be adjusted up to 5000 cycles.

We found that when using very low voltages across the bridge the sensitiveness was no longer adequate for our purpose. When measuring 1000 ohms with 4 volts, the setting of the bridge could be definitely determined to within 0.001 ohm or to one part in a million, but when the voltage was below 0.4 volt it was no longer possible to maintain a sensitiveness of 0.001%, which is the precision we desired. The best remedy seemed to be an improvement in the amplifier.

Improvements in the Amplifier.—The transformers in our two-stage amplifier, which had a step-up turns ratio of 3.5:1, were built by the General Radio Company for use in radio receiving sets and were the best commercially available at the time the bridge was originally built. Recent advances in the science of radio indicated that a substantial improvement in the performance of our amplifier could be obtained by replacing these old transformers by others of superior design.

It has been pointed out by Lord Rayleigh[3] that the telephone to be used as a detector in an alternating current bridge will have the maximum sensitiveness if it is designed so that the impedance of the telephone equals the impedance of the bridge. It is an obvious extension of this principle that when an amplifier is used between the bridge and telephone it is an advantage to have the impedance of the primary in the transformer of the amplifier match the impedance of the bridge and to have the impedance of the secondary of the transformer match the impedance of the vacuum tube which serves as its load. Since the impedance of the bridge varies with the resistance being measured and the impedance

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[3] *Lord* **Rayleigh,** *Proc. Roy. Soc. London,* 49,203 (1891).

of the primary in the transformer with a fixed inductance varies with the frequency being used, the ideal transformer would have a primary inductance which is adjustable to the most suitable value for every measurement, and a secondary which is adjustable to maintain the best step-up turns ratio.

But there are other considerations in the design or selection of transformers for this purpose. The closer the coupling between the primary and secondary, the more nearly will the effective amplification factor equal the ratio of the number of turns of winding in the secondary to that in the primary. It is also desirable to have a high step-up turns ratio, but if the turns ratio is made too great, the effective amplification factor in the transformer becomes greatly dependent on the frequency, having a sharp maximum at the natural frequency of oscillation of the secondary as determined by the inductance and distributed capacitance of the secondary and its load. The greater the resistance being measured, the sharper is the maximum of the effective amplification at the natural frequency of the oscillation of the secondary.

In the design of transformers for audio frequency amplifiers in radio receiving sets it is important that the amplification factor be as nearly as possible independent of the frequency throughout the audio frequency range to avoid distortion of music. This requirement limits the step-up ratio that can be used for this purpose. To avoid distortion, it is desirable to have the coupling between the primary and secondary as nearly perfect as possible. In recent years iron of higher permeability has become available for the core of transformers, which improves the coupling so that the step-up ratio can be increased to 6:1 without distortion, whereas a step-up ratio of 3.5 was the maximum that could be used without distortion until the better iron became available. Since we never use more than one frequency at a time it is not essential for our purposes that the effective amplification factor should be independent of the frequency and, therefore, it is possible to use greater step-up ratios.

It did not seem practicable to build a transformer which would have a primary adjustable to the most suitable inductance for each measurement and a secondary adjustable to maintain the most suitable step-up ratio and at the same time maintain a close coupling between the primary and secondary. Nor could we find available by purchase any audio frequency transformers with as low a primary inductance and as high a step-up ratio as was shown by some preliminary experiments to be desirable for our purpose. However, this difficulty was overcome through the kindness of Mr. Melville Eastham of the General Radio Company, who gave orders to have one of their standard transformers modified at the factory to serve our needs. Their transformer, Type 284,S24, which has 15,500 turns in the secondary, was modified by bringing out a tap on the primary at 400 turns (Tap I), and a tap at 1000 turns (Tap II) in addition to the original full primary winding of 2500 turns (Tap III), thus making available primary inductances of 0.3, 1.8 and 12.0 henrys, and turns ratios of 39:1 and 15.5:1 and 6.2:1, according to the tap used. In this way some adjustability is secured.

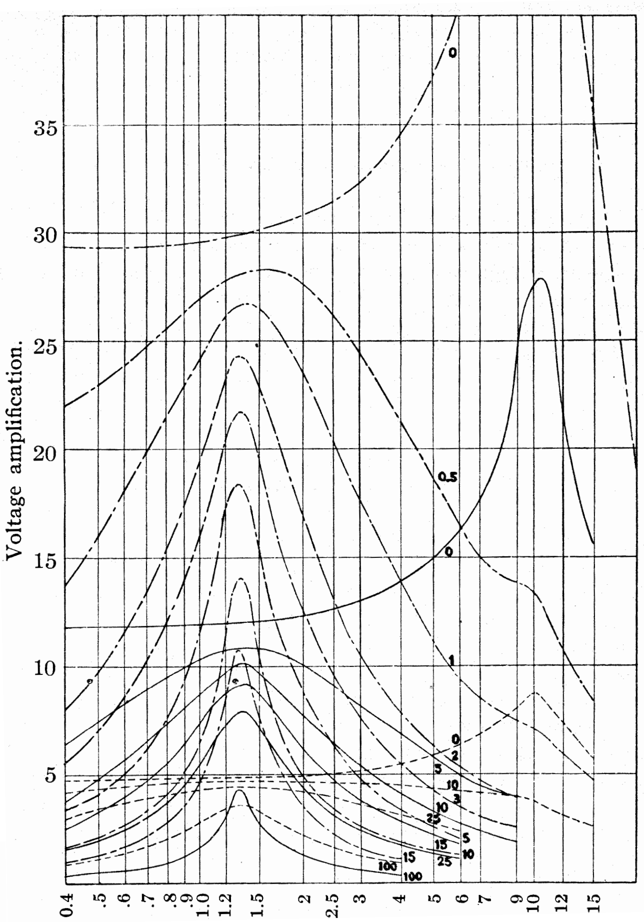
Then, through the kindness of Professor R. F. Field, who made available to us the facilities of the Cruft Laboratory and aided us by helpful suggestions, we were able to determine the actual effective amplification factor of our new modified transformer at 20 different frequencies covering the range 400 to 20,000 cycles and with various resistances covering the range 0 to 100,000 ohms in series with the primary of the transformer, using each of the three taps on the primary winding. These data are not published in full because they are applicable only to a particular instrument and are, therefore, not of general interest, but are shown graphically in Fig. 1. Extracts from these data are given in Table I to illustrate the advantages which can be gained by having a transformer which is well designed for the purpose and has taps giving some adjustability. The first column gives the resistance being measured in the bridge, R; the second column gives the corresponding effective resistance in series with the primary of the transformer, which is $(1000 + R)/2$ in our bridge with fixed ratio arms of 1000 ohms each. The body of the table gives the corresponding effective amplification factor (electromotive force at the terminals of the secondary divided by the electromotive force applied across the resistance given in the second column and the primary in series) as determined at the frequencies shown and with the taps indicated in the heading. Under the I in the heading are given the data obtained when using the first tap with 400 turns in the primary and a turns ratio of 39:1, and an inductance of 0.3 henrys; under II are the data obtained when using the second tap with 1000 turns and a turns ratio of 15.5:1 and an inductance of 1.8 henrys, and under III are the data with 2500 turns in the primary and a turns ratio of 6.2:1 and an inductance of 12.0 henrys. The figures given in parentheses are obtained by interpolation from

TABLE I

AMPLIFICATION FACTOR OF TRANSFORMER

R	$\frac{1000 + R}{2}$	500 cycles			1200 cycles			2500 cycles			5000 cycles		
		I	II	III	I	II	III	I	II	III	I	II	III
	0	*29.4*	11.9	4.8	*29.9*	12.0	4.8	*31.3*	12.6	5.0	*37.6*	15.3	5.9
0	500	*22.4*	(11.0)	(4.8)	*27.9*	(11.9)	(4.8)	*26.2*	(12.2)	(5.0)	*19.1*	(12.0)	(5.9)
1000	1000	*15.8*	(10.5)	(4.8)	*26.1*	(11.7)	(4.7)	*20.4*	(11.9)	(5.0)	*11.6*	(10.5)	(5.8)
3000	2000	*9.7*	(9.6)	(4.7)	*23.2*	(11.4)	(4.7)	*13.3*	(11.0)	(5.0)	6.3	(*8.7*)	(5.7)
5000	3000	6.6	(*8.7*)	(4.7)	*20.2*	(11.2)	(4.7)	9.5	(*10.3*)	(4.9)	4.3	(*7.4*)	(5.6)
7000	4000	5.2	(*8.0*)	(4.6)	*18.6*	(11.0)	(4.7)	7.4	(*9.7*)	(4.9)	3.3	(*6.5*)	(5.5)
9000	5000	4.1	*7.5*	4.6	*17.0*	10.7	4.7	6.1	*9.1*	4.8	2.6	*5.9*	5.3
19,000	10,000	2.0	*4.8*	4.3	*10.6*	9.7	4.6	3.2	*6.3*	4.7	1.5	3.3	*4.5*
29,000	15,000	1.3	3.3	*4.0*	8.7	*8.8*	4.6	2.2	*4.7*	4.4		2.2	*3.8*
49,000	25,000	0.8	2.0	*3.4*	5.8	*7.5*	4.4	1.3	3.1	*4.0*		1.4	*2.8*
199,000	100,000	0.2	0.5	*1.1*	1.6	3.1	*3.4*		0.8	*1.7*			

curves. The tap which should be chosen at any given resistance and frequency is shown by italicizing the highest amplification. The great improvement over the original transformer, which had a turns ratio of only 3.5 to 1, and the advantage of having several taps are quite apparent from this table and the curves of Fig. 1. Thus, for example, when measuring 1000 ohms at 1200 cycles, the lower tap (I) gives an amplification factor of 26.1, which is more than five times the amplification factor of 4.7 given by Tap III, whereas when measuring 19,000 ohms at 5000 cycles, Tap III gives an amplification factor three times as great as Tap I. In



Frequency in kilocycles, logarithmic scale.

— — — —, Tap I; ————, Tap II; - - - - - - -, Tap III.

The numbers in the figure indicate the resistance in kilohms placed in series with the primary winding.

Fig. 1.—Voltage amplification of special transformer.

the curves drawn from the complete data (Fig. 1) the natural frequency of the secondary is indicated by the maxima appearing at 1300 cycles.[4]

The selection of the most suitable tap depends both on the frequency being used and on the resistance being measured and cannot be stated in any simple manner; it can be inferred from the curves. Thus, for example, inspection of Fig. 1 shows that the curves for Tap I and for Tap II with 5000 ohms in series (which is the effective value when the resistance being measured in our bridge is 9000 ohms) cross each other at 920 cycles and again at 1800 cycles, which means that the two taps give equal amplification factors (of about 10 at 920 cycles and about 11 at 1800 cycles) with 9000 ohms in the bridge, whereas when using frequencies within this range Tap I is superior, and when using frequencies less than 920 or greater than 1800, Tap II gives the higher amplification factor.

In general, Tap I is to be preferred when measuring low resistances (3000 ohms or below) with any frequency between 500 and 3000 cycles, and can be used to advantage even when measuring high resistances if the frequency is near the natural oscillation frequency of 1300 cycles. Tap III is not to be preferred when measuring any resistance below 9000 at any frequency below 5000. When measuring high resistances, the choice between the three taps depends on the frequency. Thus, for example, when measuring 19,000 ohms in the bridge (equivalent to 10,000 ohms in series with the transformer), Tap III is best below 450 cycles, Tap II between 450 and 1150 cycles; Tap I is best in the range 1150 to 1550 cycles, which is near the natural oscillation frequency of 1300; Tap II again becomes the best in the range 1550 to 3500 and Tap III at all frequencies above 3500 cycles. It is possible to build a transformer so that it will have its natural oscillation at any frequency that may be desired.

By employing a primary winding with still fewer turns and hence a higher turns ratio than is given by Tap I—say, for example, 200 turns and a turns ratio of 78—a correspondingly greater amplification would be obtained at 1300 cycles, but calculations indicate that the curves would drop so sharply on either side of this optimum frequency when the primary was placed in series with a resistance greater than 500 ohms (the lowest limit in our bridge with fixed ratio arms of 1000 ohms each) that the advantage of a gain in the amplification factor would be offset by the narrowness of the range of frequencies over which it would be apparent.

The old transformer, originally used between the first and second stages of the amplifier was replaced by a new transformer, General Radio Type 285H, which was not on the market when the amplifier was originally built. This was an improvement because the step-up ratio was 6:1 instead of 3.5:1 and because the quality of iron is better than that in the old transformer.

The effect of these improvements was an increase of at least ten-fold in the sensitiveness of the bridge when measuring 1000 ohms with 1090 cycles and about three-fold

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[4] With little or no additional series resistance in the primary circuit a maximum appears for each tap at about 10,000 cycles. The frequency at which this maximum occurs is determined by the natural frequency of the secondary and the coefficient of coupling of the transformer. The maximum voltage rise at this point depends upon the losses in the transformer and is also greatly reduced by any resistance in series with the primary. The greatest amplification factor which we found with our transformer was nearly twice the turns ratio. In the case of Tap I the amplification factor rose to a maximum value of 70 (not shown in the figure). The high increase in amplification at this point is not available for practical use because it occurs at the extreme limit of the audible range and because it disappears as soon as any appreciable resistance is placed in the primary circuit.

when measuring 30,000 ohms. The effective amplification factor of our two-stage amplifier with these improvements varies greatly with the resistance being measured and the frequency being used, but may be estimated to be of the order of magnitude of 10^3 to 10^4.

The Use of a Wave Filter.—These changes in the amplifier brought in their train two disadvantages which were especially evident when working with low voltages. The increased efficiency of the amplifier not only magnified the desired signal but also magnified all of the disturbances, such as the so-called "tube noises," sixty-cycle hum from the electric light circuit, sparks at the commutators of motors, and at the relay control of thermostat heater, all of which were audible in the telephones. The main signal was weakened by lowering the voltage of the oscillator without any corresponding weakening of these noises, so that they became more disturbing. Fortunately the remedy was easy by using so-called wave filters. By placing a variable inductor and a variable condenser both in parallel with the telephone and then adjusting the inductance and capacitance until the relation $LC\omega^2 = 1$ is satisfied, the disturbing noises are greatly reduced with very little weakening of the desired signal in the telephone. The variable inductor was a special instrument made for us by the General Radio Company. It consisted of a coil of 2500 turns of No. 28 enamel-covered wire and a sliding E-shaped laminated iron core. The center tongue could be inserted inside the coil and the outer tongues came close to the coil on the outside. By varying the position of the core with reference to the coil, the inductance could be varied from 0.12 to 1.7 henrys. The sliding core was provided with a pointer and a calibrated scale. For a variable condenser we used a General Radio decade box with dial switches giving capacitances from 0.01 to 1.0 microfarad. With the inductor set at 0.225 henry, capacitances of 0.5 μf, 0.1 μf and 0.02 μf are suitable for 500, 1090 and 2280 cycles, respectively.

Errors at Low Voltage Due to Mutual Inductance.—The other difficulty which followed the improvement in the amplifier was the observation that when using low voltage across the bridge, the setting of the bridge at balance could be varied by merely reversing the lead wires from the amplifier to the midpoint of the bridge. We had tried this experiment on several occasions in the past without finding the effect but these experiments had been made with comparatively high voltages. We now found by experiment that with the oscillator placed about five feet from the bridge the percentage effect of reversing the amplifier lead wires (1) decreased as the voltage across the bridge was increased and became negligible (*i. e.*, less than 0.001%) when 4 volts were applied at the ends of the bridge; (2) increased with the resistance being measured in the bridge; (3) was greatest when the tap at 400 turns on the primary in the first transformer of the amplifier was in use, and least when the full

2500 primary turns were used; (4) decreased with increase in frequency; (5) could be varied by rotating the oscillator on a vertical axis and a position of minimum effect could be found; (6) could be varied by rotating the amplifier and telephones. At its worst, the effect of reversing the amplifier leads was a change of 0.45% in the bridge setting. Moreover, it was noticed that a feeble note could be heard in the telephones when the amplifier was entirely disconnected from the bridge if the oscillator was operating.[5] The note was more intense when the wave filter was connected to the telephone than when it was removed. This note was at the frequency of the oscillator and stopped when the oscillator stopped and, therefore, must have been due to a direct transfer of energy from the oscillator to the coils in the transformers of the amplifier and to the coils in the telephone and wave filter through their mutual inductance.[6] That meant that as a result of this mutual inductance between oscillator and detector there was an induced alternating electromotive force at the ends of the lead wires from the amplifier. If the bridge were at true balance so that the potential between the midpoints was exactly zero and then the lead wires were connected to the bridge, a note would be heard in the telephone, and in order to get silence in the telephone, the bridge setting would have to be changed sufficiently to give a potential between the midpoints equal in magnitude and opposite in phase to the potential induced in the amplifier. On reversing the lead wires, the bridge setting would have to be changed in the opposite direction from its true setting in order to obtain a silence in the telephones. The difference in bridge setting before and after reversing the lead wires is thus twice the error caused by the mutual inductance between oscillator and detector and the average setting would be correct. The induced electromotive force at the end of the amplifier lead wires is independent of the voltage applied to the bridge because it depends upon the variable magnetic field of the oscillating coil and is not appreciably influenced by the choice or position of the output coil. The induced electromotive force at the end of the amplifier lead wires is so small that when 4 volts is applied across the bridge it has a negligible effect, but can become appreciable as the applied voltage is lowered.

Fortunately there is a simple and effective remedy for this error by moving the oscillator to a considerable distance. When the oscillator was moved to a distance of 35 feet from the bridge, the effect of reversing

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[5] J. L. R. Morgan and O. M. Lammert, THIS JOURNAL, 48, 1231–1232 (1926), have observed a similar effect when using a Vreeland oscillator and have suggested the proper remedy of moving it to a safe distance. They say nothing about the variation of this error with the voltage used and do not suggest the use of an oscillator with a lower external field than the Vreeland oscillator.

[6] The oscillator was enclosed in a grounded metallic box and, therefore, the effect could not have been due to a variable electrostatic field.

the lead wires disappeared entirely and no note could be heard in the telephones when the amplifier was disconnected from the bridge.

Having found that the influence of the variable magnetic field of the oscillator on the detector became significant when using low voltages, it was necessary to reexamine the possibility of error due to the effect of this field on the bridge itself at the lower voltages. This was tested by changing the lead wires from the resistance box to the rest of the bridge, by reversing the lead wires from the oscillator to the bridge and by moving the oscillator. Thus, for example, measuring 30,000 ohms with 4 volts and 1090 cycles with the oscillator at a distance of five feet from the bridge, the error due to mutual inductance between the oscillator and the bridge itself was only 0.0003%. This error is negligible and, together with other similar experiments not reported in detail, confirms the conclusions drawn in the earlier work with this bridge at relatively high voltages. When the voltage was reduced to 0.01 volt without changing any of the other conditions given above, the error was 0.3%. Numerous other experiments were made to determine the influence of frequency, resistance being measured and type of resistance box, but these experiments need not be discussed in detail since the removal of the oscillator to a safe distance is a complete and perfect remedy.

If the available room does not permit moving the oscillator to a safe distance, reliable results can be obtained by taking the mean of the four readings obtained by reversing the lead wires from both the amplifier and the oscillator to the bridge. This is analogous to the usual practice of eliminating error due to thermoelectric effects in direct current measurements by means of reversing switches. Effective magnetic shielding of the oscillator is so difficult as to be hardly practicable, but the oscillator may be improved so as to reduce its outside electromagnetic field.

Grateful acknowledgment is made for an appropriation from the Milton Fund for the expenses of this research.

Summary

1. When measuring the conductance of solutions it is desirable to use a low voltage in the bridge. A modification of the oscillator to give low and controllable voltages is described.

2. The use of low voltages in the bridge diminishes the sensitiveness. The best remedy is to improve the amplifier. The principles of design of the transformer for a vacuum-tube amplifier are discussed and means of increasing the sensitiveness described.

3. The use of a wave filter in parallel with the telephone is recommended.

4. The mutual inductance between the oscillator and detector and between oscillator and bridge may cause an error in the measurement

of the conductance of solutions when low voltages are being used and means for the discovery and elimination of this error are explained.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE PREPARATION OF ANTIMONY-FREE ARSENIOUS OXIDE AND THE ESTIMATION OF MINUTE AMOUNTS OF ANTIMONY IN ARSENIOUS OXIDE

BY C. W. FOULK AND P. G. HORTON

RECEIVED MAY 15, 1929 PUBLISHED AUGUST 7, 1929

In the preparation of arsenious oxide of a high degree of purity, antimonous oxide is, by far, the most troublesome of the impurities to remove. Chapin[1] seems to be the first to call attention to the importance of this impurity and has given a method for removing it. He points out that it is impossible to accomplish this by the usual methods of purification such as recrystallization and sublimation; indeed, he states that it is entirely possible after recrystallization and sublimation to end with a "purified" arsenious oxide more impure than the original material. On the other hand a number of careful workers have regarded these methods as sufficient. Washburn,[2] in his investigation of the theory and practice of the iodimetric determination of arsenic acid, purified arsenious oxide by recrystallization from hot water and by sublimation. Baxter and Coffin[3] in their work on the revision of the atomic weight of arsenic say, "commercial C. P. arsenious oxide was recrystallized three times from dilute hydrochloric acid solution and after being rinsed with water and centrifugally drained, it was converted into arsenic acid by means of nitric and hydrochloric acid in a porcelain dish," and "arsenious oxide was twice resublimed in a current of dry air and then once recrystallized from dilute hydrochloric acid solution."

In the present investigation Chapin's work was repeated and his method found to be all he claimed for it, but inadequate if the product is to be used in atomic weight determinations or other precise work. The following proposed method is shorter and is believed to effect not only the complete removal of antimony but to a very large extent that of all other impurities as well.

Briefly stated the new method consists in converting arsenious oxide into arsenious chloride which is then repeatedly shaken out in a separatory funnel with concentrated hydrochloric acid to remove antimony. The arsenious chloride is next hydrolyzed with water to give arsenious oxide

[1] Chapin, *J. Ind. Eng. Chem.*, 10, 522–524 (1918).

[2] Washburn, THIS JOURNAL, 30, 31–46 (1908).

[3] Baxter and Coffin, *ibid.*, 31, 297 (1909).

again, which then may be subjected to the usual methods of purification such as recrystallization and sublimation.

Preparation of Arsenious Chloride.—Arsenious chloride is usually prepared by distilling a hydrochloric acid solution of arsenious oxide in a current of hydrogen chloride gas. This distillation method has been used by a large number of workers for the detection and estimation of arsenic and has been most recently studied by Roark and McDonald,[4] who give it as an effective means of separating arsenious chloride from antimony, lead, copper, zinc, iron and calcium. The present writers find, however, that unless the arsenious chloride is redistilled several times, it still contains traces of antimony.

The apparatus used for the preparation of the arsenious chloride consists of a one-liter pyrex distilling flask connected to an ordinary condenser. The condenser is provided with an adapter reaching nearly to the bottom of a 700-cc. Erlenmeyer flask used as a receiver and kept cool with ice.

In a typical experiment a solution of 150 g. of arsenious oxide in 350 cc. of concentrated hydrochloric acid was distilled in a current of hydrogen chloride gas from a suitable generator.[5] The distillate consists of two layers, oily arsenious chloride and hydrochloric acid. As distillation proceeds the distilling flask is recharged from time to time wth arsenious oxide until the desired amount of arsenious chloride is obtained.

Removal of Antimony from the Arsenious Chloride.—It was discovered that antimonous chloride is much more soluble in concentrated hydrochloric acid than in arsenious chloride and hence can easily be removed from the arsenious chloride by repeatedly shaking with portions of concentrated hydrochloric acid and subsequent separation of the two layers. So great is the difference in the solubility of antimonous chloride in the two layers that the shaking out with only a few portions of acid will remove completely a considerable amount of antimonous chloride. The procedure is as follows.

To the oily arsenious chloride in a separatory funnel is added two-thirds of its volume of concentrated hydrochloric acid and the separatory funnel shaken one minute. (The arsenious chloride layer will be diminished in volume about 10% due to its solubility in the acid.) The lower layer is now carefully drawn off and the shaking out process repeated with a fresh portion of acid until the acid layer shows no antimony by the following test.

Test for Antimony.—In order to test the acid layer for antimony it is

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[4] Roark and McDonald, *J. Ind. Eng. Chem.*, 8, 327 (1916).

[5] The hydrogen chloride generator used in this work was of the type developed by Sweeney, THIS JOURNAL, 39, 2186–2188 (1917). However, if preferred, the concentration can be kept up just as effectively by frequent additions of concentrated hydrochloric acid direct to the distilling flask.

transferred to the distilling apparatus and heated only as long as any oily arsenious chloride which it holds in solution distils over. The residue in the distilling flask is then transferred to a beaker and treated, while still hot, with hydrogen sulfide. All of the arsenic remaining in the acid is precipitated as yellow arsenious sulfide, leaving antimony in solution. The precipitate is filtered off using a double filter paper, on account of the action of the strong acid, and the filtrate diluted with three times its volume of water and again saturated with hydrogen sulfide. Under these conditions, antimony, if present, will come down as orange antimonous sulfide. In the detection of small amounts of antimony, however, the solution should be allowed to stand for a day or two after passing in hydrogen sulfide, for sometimes an orange-colored turbidity may later develop into a distinct precipitate.

The advantage of this method lies in the fact that the antimony can be removed from very large amounts of arsenious oxide, thus permitting the detection of less than 0.001%. Furthermore, when the amount of antimony is very small a fairly good quantitative determination can be made by comparing the precipitated sulfide with a series of similarly prepared precipitates of known amounts of antimony. The following is a typical experiment with the method.

By means of a dilute standard solution, **3.7** mg. of antimonous chloride was added to 300 g. of arsenious chloride, free from antimony. This is at the rate of one part of antimony in 150,000 of the chloride or in 160,000 of the oxide. The arsenious chloride was then shaken once with two-thirds of its volume of concentrated hydrochloric acid. The acid was then distilled until no more oily drops of arsenious chloride could be seen passing over.[6] The residual acid in the distilling flask was next treated with hydrogen sulfide as described above and after removing the sulfide of arsenic the solution was diluted and again saturated with hydrogen sulfide. An orange-colored precipitate was obtained slightly less in bulk than that from 3.7 mg. of antimony trichloride precipitated in the same way, that is, by saturating its concentrated hydrochloric acid solution with hydrogen sulfide, diluting and again passing hydrogen sulfide into it.

Arsenious Oxide by Hydrolysis of the Chloride.—Having obtained antimony-free arsenious chloride, the final step of converting it into the oxide is accomplished simply by allowing the chloride to run slowly from a separatory funnel into a large beaker of boiling water with vigorous stirring. On cooling, arsenious oxide separates as a fine white solid and after being filtered and washed free from acid it can be further purified if desired by recrystallization and sublimation.

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[6] The usual situation will be the detection of antimony in arsenious oxide in which case, if only a trace of antimony is suspected, 100 *g.* of the oxide is converted into the chloride by the method described above and the residual acid solution in the distillation flask is then examined for antimony.

Summary

A rapid and simple method for the preparation of antimony-free arsenious oxide has been described, and also an application of this method to the qualitative detection and rough quantitative estimation of minute amounts of antimony in arsenious oxide.

COLUMBUS, OHIO

NOTE

An Inexpensive Pyrex Conductivity Cell.—Because of its small thermal expansion and its chemical resistance, pyrex glass is most suitable for the construction of conductivity cells, hydrogen electrodes and similar apparatus. Unfortunately there is considerable difficulty in making satisfactory seals of platinum to pyrex. The writer recently required a conductivity cell which would be gas tight at five atmospheres' pressure and withstand the action of solutions of sulfur dioxide, so that a pyrex cell seemed advisable if it could be constructed. The makers of pyrex were not able to recommend any suitable method of construction but eventually by making use of the suggestions of Housekeeper[1] a suitable cell was made. As the cell is easily and cheaply made and as the construction may be readily modified for other uses, it is described herewith.

The essential point in the construction is that platinum foil, if *sufficiently* thin, may be fused firmly onto the surface of any glass. The cell used by the writer was in the form of a tube about one centimeter in inside diameter with electrodes about six by twenty millimeters spaced about ten centimeters apart. The platinum foil used was a piece recovered as salvage from a platinum resistance furnace and was in the form of a ribbon 6 mm. wide by 0.7×10^{-3} mm. thick. Somewhat heavier foil would probably be satisfactory but was not tried. A piece of this foil was cut approximately as shown at A and the 1-cm. pyrex tube had a three-millimeter side tube attached, as shown at B. The piece of foil was then put in so that the narrow tail extended into the side tube while the wider portion was bent around the inside of the large tube as shown by the dotted line in B and C. The wide tube was then heated to softening and the foil gently pressed into contact with the softened glass, a heavy piece of platinum wire being used to do the pressing. After this portion of the foil had been attached, the side tube was heated at the junction with the large one until it fell in on the foil. A gentle pinch with the tongs when the glass was soft ensured a tight joint. Enough of the tail projected

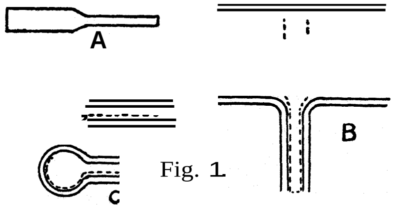

Fig. 1.

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[1] **Housekeeper,** *J. Am. Inst. Elec. Eng.*, **42,954 (1923).**

beyond the seal to make contact with mercury in the side tube, which could be lengthened and bent in any convenient way. All work was done in an ordinary blast lamp using gas and air. The foil adheres firmly to the large tube and forms an electrode which is definitely fixed. No difficulty was found when the platinum black was deposited and the cell with two such electrodes was used repeatedly at temperatures between 0 and 115° without change in constant. The lead-in seal was definitely gas tight. Although a cell of this kind might be rather difficult to make with electrodes of large area, this difficulty is readily avoided since the modern vacuum tube amplifier renders large electrodes unnecessary. The total weight of the electrode in this case was only about four milligrams, a point not without interest where cost is concerned.

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THE CHEMISTRY OF LIGNIN. III. THE DESTRUCTIVE DISTILLATION OF LIGNIN FROM CORN COBS

BY MAX PHILLIPS

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During the past few years a number of papers have appeared on the destructive distillation of lignin. All of the work thus far published has been confined to the lignin isolated from wood. Heuser and Skioldebrand[1] destructively distilled lignin isolated from spruce sawdust by the method of Willstatter and Zechmeister.[2] Their results calculated on the ash-free lignin were as follows: carbon residue, 50.64%; oil, 13.00%; acetone, 0.19%; methanol, 0.90%; acetic acid, 1.09%.

Hagglund[3] distilled lignin isolated from pine wood by the hydrochloric acid method of Willstatter and Zechmeister and obtained 45% carbon residue, 9.6% oil, 0.10% acetone, 0.67% methanol and 0.64% acetic acid.

Fischer and Schrader[4] distilled Willstatter lignin and obtained 13.2% aqueous distillate, 12.5% oil, 57.2% carbon residue and 17.0% gas (obtained by difference). It was found that 16.4% of the oil dissolved in sodium carbonate and 33.9% in sodium hydroxide solution.

[2] Canadian Pulp and Paper Association Research Fellow.

[1] Heuser and Skioldebrand, *Z. angew. Chem., I,* 32, 41 *(1919).*

[2] Willstätter and Zechmeister, *Ber.,* 46, 2401 (1913).

[3] Hagglund, *Arkiv. far Kemi, Min. och* Geol., 7, 1 (1918); *Chem. Zentr.,* 90, III, 186 (1919).

[4] Fischer and Schrader, *Abhand. Kohle,* 5, 106 (1920).

Tropsch[5] destructively distilled commercial Willstatter lignin under reduced pressure (1–2 mm.) and obtained **14.2%** aqueous distillate, 10.2% oil and **53.8%** carbon residue. The oil contained 37.5% phenolic compounds.

Pictet and Gaulis[6] distilled under reduced pressure commercial Willstatter lignin isolated from fir. They obtained 15% oil, 21% aqueous distillate and 52% carbon residue. No examination of the aqueous distillate was made. The oil was extracted with 10% sodium hydroxide, in which 89% dissolved. In the alkali-soluble fraction eugenol was identified. The alkali-insoluble fraction was separated by means of liquid sulfur dioxide into saturated and unsaturated hydrocarbons. In the fraction containing the saturated hydrocarbons melene was identified.

The present paper contains results on the destructive distillation of lignin from corn cobs. The lignin used in the destructive distillation experiments was prepared by three different methods: the alkali method, the fuming hydrochloric acid method of Willstatter and the 72% sulfuric acid method. The results obtained tend to support the claim that the lignin fraction obtained from corn cobs by the alkali method is quite different in composition from that obtained by either the Willstätter or the 72% sulfuric acid method. While some differences in the results were noted also in the lignin prepared by the two last mentioned methods, the principal difference was between the alkali lignin on the one hand and the Willstatter and **72%** sulfuric acid lignins on the other.

The results recorded in the literature on the destructive distillation of lignin are limited entirely to lignin isolated from wood by the Willstatter method, and in comparing those results with that recorded in this paper on the lignin isolated from corn cobs by the same method, it is observed that the values, with exception of that recorded for the yield of acetone, are of the same general order of magnitude. The yield of acetone was much higher in the case of lignin isolated from corn cobs than that recorded in the literature on lignin from wood (compare Tables I and II). Whether this may be attributed to an essential difference in the composition of the lignins from the two sources, or is due to some impurity present, it is difficult to state, considering our present fragmentary knowledge of the chemistry of lignin.

Experimental

Preparation of Lignin by the Alkali Method.—The corn cobs were treated with six times their weight of 2% sodium hydroxide solution and heated in an autoclave for eight hours under 25 pounds' pressure. The alkaline liquors were then drained off, the cobs were washed with a stream of water and the wash water was added to the alkaline liquor. This liquor was filtered and then made acid with an excess of either 50% sulfuric

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[5] Tropsch, *Abhand. Kohle*, **6**, 293 (1921).

[6] Pictet and Gaulis, *Helv. Chim. Acta*, 6,627 (1923).

acid or with concentrated hydrochloric acid. This was heated to boiling and boiled for half an hour, allowed to cool to room temperature, then centrifuged in a basket centrifuge and finally dried at 100°. The yield amounted to from 4 to 5% of the weight of the cobs taken. The lignin thus obtained was free from cellulose and when distilled with 12% HCl, according to the Official A. O. A. C. Method,[7] gave a precipitate with phloroglucinol corresponding to 2.45% pentosans as calculated by the Krober formula.

A methoxyl determination was made according to the Kirpal and Buhn[8] modification of the Zeisel[9] method. The iodine was, however, determined gravimetrically as silver iodide instead of volumetrically as recommended by Kirpal and Buhn.

Anal. Subs., 0.4682, 0.6678 (calcd. on ash-free basis): AgI, 0.5075, 0.7223. Found: OCH_3, 14.31, 14.28.

Preparation of Lignin by the Fuming Hydrochloric Acid Method.—The procedure recommended by Willstätter and Kalb[10] was followed, except that a longer period was allowed for the hydrochloric acid to act upon the corn cobs. Corn cobs (200 g.) ground to pass through a 20-mesh sieve were mixed with four liters of fuming hydrochloric acid (d = 1.21 at 15°) and allowed to stand at room temperature for twenty-four hours. The flask containing the reaction mixture was shaken from time to time. To the reaction mixture 1300 g. of crushed ice was added and it was allowed to stand for another twenty-four hours. It was then diluted further with six liters of water, filtered on a Buchner funnel using a woolen filter cloth in place of filter paper, and washed with water until the wash water no longer gave a test for the chlorine ion with silver nitrate. The product, which was almost black in color, was dried at 100°; yield, 23.5–25% calculated on the weight of the cobs used. It contained 1.05% of ash.

A methoxyl determination made on this material gave the following results: Subs., 0.3088, 0.3236 (calcd. on ash-free basis): AgI, 0.1988, 0.2123. Found: OCH_3, 8.50, 8.66.

Preparation of Lignin by the 72% Sulfuric Acid Method.—Corn cobs, ground to pass through a 20-mesh sieve were mixed with four liters of 72% sulfuric acid and allowed to stand at room temperature for thirty-six hours. The reaction mixture was shaken from time to time. At the end of the thirty-six hour period a sample of the reaction product was examined microscopically in parallel polarized light with crossed nicols and was found to be free from doubly refractive substances.[11] The reaction product was diluted with four times its volume of water, heated to boiling and maintained at this temperature for one hour. The product was filtered off and washed with hot water until free from sulfuric acid. It was dried at 100°. The yield amounted to 19% of the weight of the cobs. It contained 1.10% of ash.

A methoxyl determination made on this material gave the following results. Subs., 0.3083, 0.3111 (calcd. on ash-free basis): AgI, 0.2242, 0.2253. Found: OCH_3, 9.61, 9.57.

Apparatus Used.—The destructive distillation experiments were conducted in a copper retort which was heated in a bath consisting of a eutectic mixture of sodium-potassium nitrate. The retort was connected to a weighed distilling flask which served as a

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[7] "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," Washington, D. C., 1925, p. 120.

[8] Kirpal and Buhn, Ber., 47, 1084 (1914); *Monatsh.*, 36,853 (1915).

[9] Houben, "Die Methoden der Organischen Chemie," Georg Thieme, Leipzig, 1923, Vol. III, p. 144.

[10] Willstätter and Kalb, *Ber.*, 55, 2640 (1922).

[11] The microscopic examinations were made by Mr. George L. Kennan of the Microchemical Laboratory of the Food, Drug and Insecticide Administration.

condenser and receiver. The distilling flask was cooled with water and connected in series to another receiver which was cooled with ice.

Experimental Procedure and Analysis.—In each experiment 50 g. of lignin was used. After several preliminary tests it was determined that 380–400° was the optimum temperature for carrying out the destructive distillations, which usually required about four hours to complete. The distillate was collected in a weighed receiver and its weight determined. The result thus obtained is recorded in Table I, under the heading "Total Distillate." The oily portion was separated mechanically from the aqueous distillate and weighed, and the weight of the aqueous distillate obtained by difference. The amount of gaseous substances produced was obtained by deducting the combined weight of "Total Distillate" and non-volatile carbon residue left in the retort from the weight of the original lignin.

The aqueous distillate was purified with activated charcoal (Darco) as recommended by Stritar and Zeidler,[12] filtered into a 200- or 250-cc. volumetric flask and made up to the mark. The percentage of methanol in this solution was determined by the method of Stritar and Zeidler.[12] The acetone was determined by the Messinger[13] method, which was carried out as follows: twenty cc. of the solution to be analyzed was measured into a 300-cc. glass-stoppered Erlenmeyer flask. To this was added 20 cc. of N sodium hydroxide solution and an excess (about 50%) of $N/10$ iodine solution. This was well shaken, allowed to stand for one hour and **20.3** cc. of N hydrochloric acid added; the excess of iodine was determined by titration against $N/10$ sodium thiosulfate solution.

The organic acids in the aqueous distillate were determined either by titration against $N/10$ sodium hydroxide solution or, when the color of the solution did not permit direct titration, by boiling an aliquot of the aqueous distillate with an excess of barium carbonate for about one hour under the reflux condenser, filtering off the unused barium carbonate and determining the barium in the filtrate gravimetrically as barium sulfate. In either case the results were calculated as acetic acid. The results obtained are recorded in Table I.

It will be observed from Table I that the results are quite different in the case of alkali lignin than that of the lignin isolated by either the Willstatter or 72% sulfuric acid method. The yields of aqueous distillate and oil were much higher, whereas the yields of carbon residues were lower in the experiments with alkali lignin than with lignin prepared by the other two methods. In this connection it may also be stated that the carbon residues from alkali lignin were light and spongy, whereas those from the other two preparations were generally obtained either in the form of hard lumps or as a black powder.

As regards the composition of the aqueous distillate, it will be observed from Table I that a higher methanol yield but lower acetone and acetic acid yields were obtained from alkali lignin than from Willstatter and 72% sulfuric acid lignin. The higher methanol yield from alkali lignin is undoubtedly due to its higher methoxyl content. The low yield of acetic acid obtained from alkali lignin may be explained by the fact that in preparing lignin by this method deacetylation occurs. This has been shown by Pringsheim and Magnus[14] and confirmed repeatedly in this

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[12] Stritar and Zeidler, *Z. anal. Chem.*, *43*, 387 (1904).

[13] Messinger, *Ber.*, **21**, 3366 (1888).

[14] Pringsheim and Magnus, *Z. physiol. Chem.*, **105**, 179 (1919).

TABLE I

RESULTS ON DESTRUCTIVE DISTILLATION OR LIGNIN FROM CORN COBS

In experiments marked "A"—alkali lignin was used. In experiments marked "B"—Willstatter lignin was used. In experiments marked "C"—lignin isolated by 72% H_2SO_4 method was used.

Expt. no.	Lignin Quantity used (grams)	Lignin Ash-free lignin (grams)	Total distillate Grams	Total distillate Calcd. on ash-free lignin %	Aqueous distillate Grams	Aqueous distillate Calcd. on ash-free lignin %	Oil Grams	Oil Calcd. on ash-free lignin %
1-A	50	49.1	16.58	33.7	7.51	15.2	9.07	18.5
2-A	50	49.1	16.10	32.7	7.61	15.5	8.49	17.3
3-A	50	49.1	16.28	33.1	7.55	15.4	8.73	17.8
4-A	50	49.1	16.34	33.2	7.86	16.0	8.48	17.2
5-B	50	49.48	12.90	26.0	8.90	17.9	4.0	8.0
6-B	50	49.48	9.60	19.4	6.10	12.3	3.5	7.0
7-C	50	49.45	10.48	21.2	7.51	15.1	2.97	6.0
8-C	50	49.45	12.19	24.6	7.37	14.9	4.8	9.7

Carbon residue Grams	Carbon residue Calcd. on lignin used %	Gas (by difference) Grams	Gas (by difference) Calcd. on ash-free lignin, %	Components of aqueous distillate: Acetone Grams	Acetone Calcd. on ash-free lignin, %	Methanol Grams	Methanol Calcd. on ash-free lignin, %	Acid Calcd. as acetic acid, grams	Acid Calcd. on ash-free lignin, %
26.2	52.4	6.3	12.8	0.0408	0.08	0.9692	1.97	0.0247	0.05
26.2	52.4	6.8	13.8	.0630	.12	.9642	1.96	.0264	.05
26.0	52.0	6.8	13.8	.0750	.15	.8959	1.82	.0336	.06
26.0	52.0	6.8	13.8	.0878	.17	.8963	1.82	.0250	.05
29.5	59.0	7.6	15.3	.3000	.60	.3480	0.70	.5702	1.15
29.0	58.0	11.4	23.0	.2718	.54	.3466	.70	.5160	1.04
31.5	63.0	8.02	16.2	.4420	.89	.4280	.86	.4700	0.95
34.0	68.0	3.81	7.7	.5877	1.18	.5950	1.2	.4348	.87

Laboratory. The writer has always obtained negative results when making acetyl determinations by the Perkin[15] method upon alkali lignin isolated from corn cobs.

The yields of acetone obtained from alkali lignin are of the same general order of magnitude as that reported on Willstatter lignin from wood by Heuser and Skioldebrand[1] and by Hägglund.[3] However, the acetone yields from the lignin prepared from cobs by the Willstatter and by the 72% sulfuric acid methods were much higher than those recorded in the literature.

For purpose of comparison, the data reported in the literature on the destructive distillation of lignin are recorded in Table II.

The oil obtained in the four distillation experiments with alkali lignin (24.6 g.) was dissolved in ether and successively extracted with 5% sodium bicarbonate solution and 5% potassium hydroxide solution. The ether solution which had thus been extracted was dried over anhydrous calcium chloride, the ether was removed by evaporation and the residue was weighed. The result thus obtained is recorded in Table III under "Hydrocarbons and Inert Compounds." The potassium hydroxide and so-

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[15] Perkin, *Proc. Chem. Soc.*, 20, 171 (1904).

TABLE II

RESULTS ON DESTRUCTIVE DISTILLATION OF LIGNIN REPORTED BY VARIOUS INVESTIGATORS

Investigators	Source of lignin	Method used for isolating the lignin	Carbon residue %	Oil %	Aqueous distillate %	Gas (by difference) %	Acetone %	Methanol %	Acetic acid %
Heuser and Skiöldebrand	Spruce	Fuming HCl method of Willstätter	50.64	13.0	..	..	0.19	0.90	1.09
Hagglund	Pine	Fuming HCl method of Willstätter	45.0	9.6	..	..	0.10	0.67	0.64
Fischer and Schrader	Coniferous wood	Fuming HCl method of Willstätter	57.2	12.5	13.2	17.0	. .	. .	. .
Tropsch	....	Fuming HCl method of Willstätter	53.8	10.2	14.2	. .	. .	. .	. .
Pictet and Gaulis	Fir	Terrise and Levy Patent (essentially the Willstätter method)	62.0	15.0	21.0	. .	. .	. .	. .

dium bicarbonate extracts were acidified and extracted with ether. The ether solutions were dried over anhydrous sodium sulfate, the ether was distilled off and residues weighed. The results obtained are given in Table III.

TABLE III

ANALYSIS OF OIL

	Percentage of oil by weight
Acids	8.6
Phenols	84.0
Hydrocarbons and neutral compounds	7.2

The phenolic portion of the oil was repeatedly fractionated. After several fractionations it was resolved into three fractions: 204–208°, 208–225° and 225–240°. Fraction 204–208° gave an orange color with ferric chloride solution. A picrate prepared according to the directions given in Mulliken, Vol. 1, page 91, melted at 85°. This fraction, therefore, consisted principally of guaiacol. It amounted to 2.3% of the weight of lignin distilled. Fraction 208–225° was not identified. Fraction 225–240° gave a greenish-blue coloration with ferric chloride solution. An alcoholic solution of it gave a blue color with ferric chloride. A benzoyl derivative prepared from this fraction melted at 70.5°. This fraction, therefore, contained eugenol.

Summary

Lignin prepared from corn cobs by the alkali method, the fuming hydrochloric acid method of Willstatter and by the 72% sulfuric acid method, was subjected to destructive distillation under ordinary atmospheric pressure and at a temperature of 380 to 400°. From the alkali lignin the following results, representing the average of four experiments (calculated on the basis of ash-free, dry lignin) were obtained: aqueous distillate, 15.5%; water-insoluble oily distillate, 17.7%; carbon residue

(calculated on the quantity of lignin used), 52.2%; gas, 13.5% (by difference); acetone, **0.13%**; methanol, 1.9%; water-soluble acids (calculated as acetic acid), **0.05%.** The oily distillate analyzed as follows: (The results are expressed as per cent. by weight of the oil) acids, 8.6%; phenols (fraction soluble in 5% KOH solution and insoluble in 5% $NaHCO_3$ solution), 84.0%, hydrocarbons and neutral compounds, 7.2%. In the phenolic portion of the oil guaiacol and eugenol were identified.

In the case of the Willstatter lignin and the lignin prepared by the 72% sulfuric acid method, the percentage of aqueous distillate was about the same as that obtained from alkali lignin, whereas the oily distillate was only about one-half. The percentages of carbon residues obtained from the Willstatter lignin and from the 72% sulfuric acid lignin were considerably greater than that obtained from alkali lignin. The percentages of acetone and acetic acid obtained were considerably greater in the case of the Willstatter and the 72% sulfuric acid lignin than in the alkali lignin, whereas, the percentage of methanol was less. This higher percentage of methanol is probably due, in part, to the greater methoxyl content of alkali lignin than that of Willstatter and 72% sulfuric acid lignin. A possible explanation for the lower yield of acetic acid obtained from alkali lignin is presented.

WASHINGTON, D. C.

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

NEW CONDENSATIONS OF KETONES WITH PHENOLS. III. CONDENSATION PRODUCTS OF MESITYL OXIDE AND MONOHYDROXYBENZENES

BY JOSEPH B. NIEDERL[1]

RECEIVED AUGUST 17, 1928 PUBLISHED AUGUST 7, 1929

Introduction

In continuation of the studies of the condensation possibilities of ketones with phenols, as begun with the condensation system phorone–cresols,[2] the condensation systems of mesityl oxide with monohydroxybenzenes were investigated. The discussion of the results of these investigations is the purpose of this communication.

Theoretical Part

By treating a molar mixture of mesityl oxide and a monohydroxybenzene with concentrated sulfuric acid in the cold, condensation products are ob-

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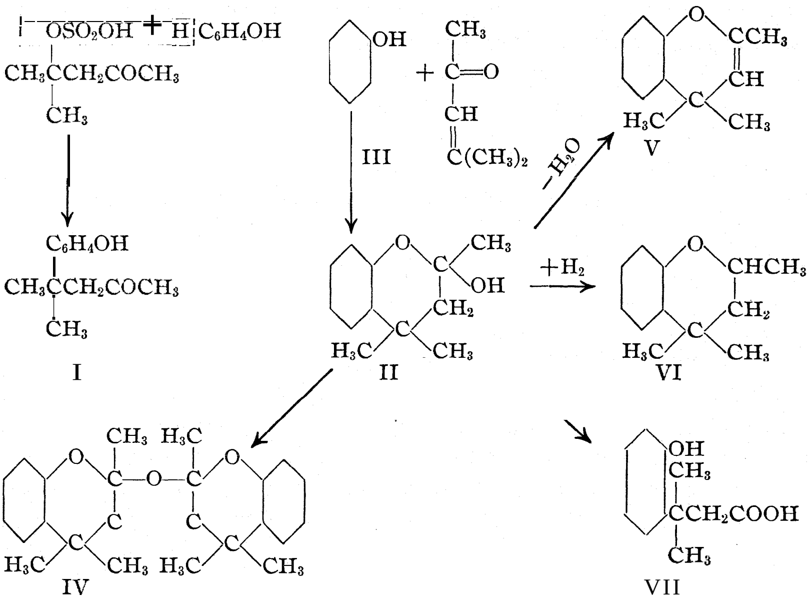
[1] In collaboration with Nathan Ambinder, Richard Casty, De Witt C. Knowles, Irving Rappaport and William Saschek.

[2] Niederl, THIS JOURNAL, 50, 2230 (1928); Niederl and Casty, *Monatsh.*, 51, 1028 (1929).

tained which appear to be chromanols (II) and dichromanyl ethers (IV) and their formation may be interpreted either (as illustrated in the chart) that from the mesityl oxide sulfuric acid (I) the phenyl-substituted isobutyl methyl ketone (I) is formed, which then changes into the isomeric chromanol (II), a behavior which is in harmony with observations made on structurally related substances,[3] or that their formation may have taken place in the form of a direct addition (III). In most cases, however, the reaction did not end with the formation of the chromanols, but dehydration occurred and the dichromanyl ethers (IV) resulted.

Both the chromanols (II) (they are really semi-acetals) and the dichromanyl ethers (IV) (di-acetals) are very stable toward alkali but are quite sensitive toward acids, as indicated by the formation of colored decomposition products.*



On reduction (with hydriodic acid or zinc and hydrochloric acid) they are reduced to the corresponding chromanes (VI), while on distillation they lose one mole of water and form the corresponding chromenes (V), a behavior which is in accordance with similar phenomena observed on structurally related chromanols.[5]

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[3] Harries and Busse, *Ber.*, 28, 502 (1895); 29, 376 (1896); Zincke and Hohorst, *Ann.*, **353**, 377 (1907).

[4] Lowenbein, Pongrácz and Spiess, *Ber.*, 57, 1517 (1924); Arndt and Pusch, *ibid.*, **58**, 1648 (1925).

[5] Heilbron and Hill, *J. Chem. Soc.*, **131**, 2005 (1927); Lowenbein and Rosenbaum, *Ann.*, **448**, 223 (1926).

The oxidation with chromic acid anhydride in glacial acetic acid yielded phenyl-substituted *iso*valeric acids (VII), the formation of which may also be regarded as a further support of the assigned formulas.

Experimental Part

For the preparation of practically all the condensation products to be described later the following process was used. To a molar mixture or solution of the monohydroxybenzene and mesityl oxide, one mole of concentrated sulfuric acid was added in small amounts. The temperature throughout the addition was kept at 0° to avoid objectionable tar formation. The mixture turned dark red. The flask containing the reaction mixture was then closed with a stopper having a calcium chloride drying tube attached, to prevent any absorption of moisture. To eliminate any further possibility of a violent after-reaction, the flask was kept in a water-bath the temperature of which was maintained at 15 to 20°.

On standing for a week the reaction mixture became solid, or at least semi-solid, indicating positive condensation. When no condensation took place (as in the case of ethers and esters), the material remained a mobile liquid, or in the same state as it had been originally.

Now cold water was added to the reaction mixture in excess, in order to extract the sulfuric acid and the phenylsulfonic acids that may have been formed in the reaction as by-products. After repeated washings of the reaction material with cold water, it was finally heated on a water-bath and treated with a large excess of hot water with constant stirring, in order to make the extraction of water-soluble products complete. At the temperature of the boiling water-bath the material usually melted. After cooling the water was decanted off. This operation was repeated until the wash water remained clear. At this stage the reaction product has the appearance of a dark, solid or semi-solid, gummy mass.

In the next step the solubility of the condensation product in 10% aqueous sodium hydroxide solution is tested. If it is soluble, the entire material is dissolved in hot 10% aqueous sodium hydroxide solution and filtered quickly while hot. The filtrate is then cooled to 0° or lower and ice-cold, dilute (5%) sulfuric acid added in small amounts. Since these condensation products are very sensitive toward acids (on account of the formation of colored decomposition products), any excess of the acid must be avoided and it is even favorable to keep the mixture just slightly alkaline. The condensation product (phenyl-substituted methyl isobutyl ketones or some chromanols) precipitates out and is filtered, or the supernatant liquid is decanted off and the residue repeatedly washed until free from inorganic substances. The product at this point should be light to golden yellow in color.

If the condensation product is insoluble in 10% aqueous sodium hydroxide solution (dichromanyl ethers), it is treated with a hot aqueous sodium or potassium hydroxide solution (10%) until the material acquires a yellow color. It is then cooled, whereby the product solidifies, and then well washed with hot and with cold water until free from alkalies. At this point, also, the product should have a bright yellow color.

The condensation products (the chromanols and the dichromanyl ethers) are insoluble in hot and cold water; some are soluble in dilute aqueous sodium hydroxide solution; they are soluble in alcohol, ether, chloroform, carbon tetrachloride, acetone, glacial acetic acid, benzene, petroleum ether, pyridine and concentrated sulfuric acid (deep red color). Since the products are quite difficult to crystallize, no general rule for their crystallization can be given, but it has been found that alcohol, ether, pyridine, benzene and ligroin are the most suitable crystallizing media.

In carrying out blank experiments under strictly similar reaction conditions with either mesityl oxide and sulfuric acid, or the monohydroxybenzenes and sulfuric acid, no such condensation products could be obtained.

TABLE I

COMPOUNDS PREPARED, MELTING POINTS AND ANALYTICAL DATA

	Mesityl oxide and	M. p., °C.	Analyses,[a] %		
Chromanol-2			Calcd.	Found	
2,2,4-Trimethyl-	Phenol	89	C, 75.00	75.15	75.20
$C_{12}H_{16}O_2$			H, 8.33	8.12	8.22
Dinitro derivative, $C_{12}H_{14}N_2O_6$		155	N, 9 92	9.74	9.78
7-Nitro-2,2,4-trimethyl-, $C_{12}H_{15}NO_4$	m-Nitrophenol	148	N, 5.91	5.88	5.95
6-Nitro-2,4,4-trimethyl-, $C_{12}H_{15}NO_4$	*p*-Nitrophenol	132	N, 5.91	5.87	5.89
2,4,4,8-Tetramethyl-	o-Cresol	120	C, 75 72	75.92	
$C_{13}H_{18}O_2$			H 8.73	8.50	
2,4,4,7-Tetramethyl-	Trinitro-*m*-cresol	120	C, 75.72	75 83	75.85
$C_{13}H_{18}O_2$			H, 8.73	8.90	8.88
Chromanyl ether-2					
Di-(2,4,4,7-tetramethyl)-	*m*-Cresol	58	C, 79.18	79.05	
$(C_{13}H_{17}O)_2O$			H, 8.54	8.32	
Tetranitro derivative $(C_{13}H_{15}N_2O_5)_2O$		145	N, 9 77	10.08	
Di-(2,4,4,6-tetramethyl)-	*p*-Cresol	57	C, 79 18	79.10	
$(C_{13}H_{17}O)_2O$			H, 8.54	8.22	
Tetranitro derivative $(C_{13}H_{15}N_2O_5)_2O$		167	N, 9.77	9 77	
Di-(5-chloro-2,4,4,7-tetramethyl)-	6-Chloro-m-cresol	71	C, 67.53	67.73	67.95
$(C_{13}H_{16}ClO)_2O$			H, 6.92	7 0 5	7.11
Di-(2,4,4,6,8-pentamethyl)-	1,3-Dimethyl-4-	Semi-			
$(C_{14}H_{19}O)_2O$	hydroxybenzene	solid	.....	...	
Tetranitro derivative $(C_{14}H_{17}N_2O_5)_2O$		155	N, 9 6 2	9.19	9.29
Di-(2,4,4,8-tetramethyl-*iso*propyl)-	Carvacrol	Semi-			
$(C_{16}H_{23}O)_2O$		solid	.....	...	
Dinitro derivative $(C_{16}H_{22}NO_3)_2O$		185	N, 4 93	4 68	5 24
Di-(2,4,4,5-tetramethyl-8-*iso*propyl)-[b]	Thymol	136	C, 80.33	80.30	80.4
$(C_{16}H_{23}O)_2O$			H, 9.62	9.26	9.5
Dinitro derivative $(C_{16}H_{22}NO_3)_2O$		201	N, 4.93	5 0 5	5.15

[a] All of the quantitative determinations were carried out micro-analytically according to Pregl, "Quantitative Organic Micro-Analysis," P. Blakiston's Son and Co., Philadelphia, 1924.

[b] Molecular weight: calcd., 478; found, 466, 505,484.

Summary

1. New condensations of unsaturated ketones with phenols were investigated and the condensation system monohydroxybenzenes–mesityl oxide was studied. The condensation products are apparently chromanols or dichromanyl ethers, respectively.

2. These condensation products are valuable intermediates for the preparation of phenyl-substituted aldehydes and acids (by oxidation) and by the distillation of the acids or their sodium salts so obtainable, the corresponding isopropyl and isobutyl phenols can be synthesized; hence the condensation process just described furnishes an additional means for the introduction of alkyl groups into the benzene ring.

Further investigations of the condensation possibilities of unsaturated ketones, unsaturated aldehydes, unsaturated acids and unsaturated alcohols with phenols (both mono- and polyhydroxylic, mono- and polycyclic), aromatic hydroxy-aldehydes and aromatic hydroxy-acids are being carried on and positive results already have been obtained.

NEW YORK CITY

[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE REACTIONS OF ALLYL ALCOHOL OVER ALUMINUM AND ZINC OXIDE CATALYSTS

BY PAUL E. WESTON AND HOMER ADKINS

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F. H. Constable[1] suggested that propionaldehyde was formed from allyl alcohol over copper through the intramolecular rearrangement of allyl alcohol, as in Equation 1.

$$CH_2{=}CHCH_2OH = CH_3CH_2CHO \qquad (1)$$

He demonstrated that it was not formed according to Equations 2 and 3

$$CH_2{=}CHCH_2OH = CH_2{=}CHCHO + H_2 \qquad (2)$$

$$CH_2{=}CHCHO + H_2 = CH_3CH_2CHO \qquad (3)$$

Evidence was presented in a previous paper[2] from this Laboratory that part if not all of the propionaldehyde formed over a zinc oxide catalyst from allyl alcohol resulted from the reduction of acrolein by allyl alcohol as in Equation 4

$$CH_2{=}CHCHO + CH_2{=}CHCH_2OH = CH_3CH_2CHO + CH_2{=}CHCHO \qquad (4)$$

It now seems certain that over alumina propionaldehyde is formed from allyl alcohol through intramolecular rearrangement. When allyl alcohol was passed over alumina at 330° gas was formed rapidly for a few minutes but the action died off within ten minutes after less than

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[1] Constable, *Proc. Roy. Soc. London*, **113A**, 254 (1926).

[2] Weston and Adkins, THIS JOURNAL, 50, 1930 (1928).

200 cc. of gas had been produced. The catalyst was then dark colored but produced propionaldehyde at a fair rate. No acrolein was formed at any time and the amount of hydrogen produced was no more than a total of 10 cc. Moreover, there is no evidence that alumina will dehydrogenate any alcohol at 330°. Almost the only conceivable mechanism for the formation of propionaldehyde is that suggested by Constable (Equation 1).

The amounts of propionaldehyde formed in the interval from 40 to 110 minutes when 50 cc. of allyl alcohol per hour was passed over 0.6 cc. of various alumina catalysts at 330° is Catalyst (A), 1.48 g., (B), 0.43 g. and (C) 2.14 g. If the catalyst was previously dried for ten hours at 125° or for four hours at 420°, the amounts of propionaldehyde formed were as follows: Catalyst (A), 5.11 g., (B), 1.17 g. and (C), 3.62 g. If the alcohol was passed at a rate of 20 cc. per hour the amount of propionaldehyde was reduced to 1.12 g. for Catalyst (B) and to 2.97 g. for Catalyst (C). The relative reactivities of these catalysts are about the same as those shown for ethylene production from ethyl alcohol at 330°.

For the reasons given in the introduction to our previous paper we were interested in determining the effect of modifications of the catalyst upon its activity and upon the ratio of the reaction products. The method of experimentation has already been described on pages 1931, 1932 and the first paragraph on page 1934 of our previous paper. An abstract of the experimental results obtained in using 13 different zinc oxide catalysts is given in the table.

Table I

Formation of Propionaldehyde and Acrolein on Various Zinc Oxide Catalysts for the Period from 40 to 110 Minutes

	From zinc oxalate			From zinc hydroxide					From zinc oxalate plus 1% (molar) promoter				
Catalyst	1A	2A	3A	4B	5B	6B,	7B	8B	9C, H_3BO_3	10D CrO_3	11E NaOH	12F H_2SO_4	13G H_2WO_4
Aldehydes, g	1 58 (1 13)	1 48	1 56	1 25	1 71	1 66	2 64	2 02	1 73 (1 26)	2 48 (2 08)	2 75 (1 91)	1 14 (0 93)	3 10
Acrolein (molar), %	11 5, (14 0)	11 0	10 3	7 6	6 3	5 3	4 2	7 4	9 3 (10 1)	6 3 (8 5)	8 0 (9 4)	10 4, (11 2)	6 5
Acrolein, g	0 16 (0 15)	0 16	0 15	0 09	0 09	0 09	0 11	0 15	0 16 (0 12)	0 16 (0 17)	0 22 (0 17)	0 12 (0 16)	0 20

The figures in parentheses are for a rate of flow of 20 cc. of allyl alcohol per hour. **All** other figures are for a rate of flow of 50 cc. per hour of the alcohol. **All** experiments were duplicated at least once, 0.6 cc. of catalyst, as determined from the actual dimensions of the pellets, being used at **330°**.

An accurate comparison of catalysts as to their effect upon a given reaction depends upon obtaining a standard catalyst which is easily and precisely reproducible. For reasons which will be more fully developed in another paper by Dr. Paul E. Millington, the zinc oxide obtained through the thermal decomposition of zinc oxalate was chosen as a standard.

The first three experiments serve to illustrate the reproducibility of the catalysts from zinc oxalate. Three entirely different preparations were used, two of them from zinc carbonate and oxalic acid (1A and 3A), and one from zinc sulfate and oxalic acid (2A). The total activity, as measured by the total amounts of aldehydes formed, ranged from 1.48 to 1.58 g., while the percentage of acrolein ranged from 10.3 to 11.5%. The variation in the percentage of acrolein in duplicate experiments was generally less than 0.7% and rarely more than 1.0%. The amounts of aldehydes produced could not be checked so closely because the volume of the catalyst, and the activity of separate portions, varied slightly.

Catalysts prepared from zinc hydroxide could not be duplicated. (This fact is treated more fully in a paper by Dr. Paul E. Millington.) Even though two preparations were treated as nearly alike as possible, they would give different results, both in the amount of reaction and in the ratio of the two reactions. In Expts. 4 and 5 the catalysts were prepared in the same manner, yet the total activity was 1.25 and 1.71 g., and the percentage of acrolein was 7.5 and 5.3%, respectively. The method of washing the catalyst did not change its properties, because in Expt. 5 the catalyst was washed by repeatedly dropping the hot oxide into boiling water and in Expt. 6 all of the washing was done with cold water, yet they are alike both in activity (1.71–1.66 g.) and in percentage of acrolein (5.3–5.3%). However, the amount of washing seems to be important. The catalysts in Expts. 4, 5 and 6 were washed until they were free from sulfates. The catalyst used in Expt. 7 was washed only twice, and it contained considerable sulfate. This catalyst gave irregular results, the activity being very high (2.64 compared to 1.70 g.), and the percentage of acrolein being quite low (4.2%). These results are probably due to the large amount of sodium sulfate which it contained. Experiment 8 shows the results obtained with a catalyst which should be exactly like 3B, but which was prepared by Dr. Millington. This gave a different percentage of acrolein (7.4% instead of 5.3%) and had an entirely different activity (2.02 g. compared to 1.66 g.). Regardless of the variation in different catalysts from zinc hydroxide, the results were entirely different from those of the oxides from zinc oxalate. The catalysts from the hydroxides gave from 4.2 to 7.5% of acrolein, while those from the oxalates gave from 10.3–11.5% of acrolein.

Having chosen one catalyst as a standard, catalysts were prepared in which various acidic and basic compounds were incorporated, and then the ratio of the reactions was determined as usual. These promoters were chosen because of their known activity in modifying the ratio of dehydration to dehydrogenation of alcohols and having in mind the hypothesis of Professor Hugh Stott Taylor (Colloid Symposium Monographs, 4, 19 (1926), Chemical Catalog Co., Inc., New York City) with respect to the effect of acid and alkaline promoters or poisons. In all but one case the promoted catalysts had a greater activity than the standard catalyst, and also the ratios of the reactions were different. In view of the fact that the rate of alcohol flow and the activity of the catalyst affect the ratio of the reactions, it may seem at first that the selective activation is only apparent and not real. An examination of the data in the table and a consideration of the following reasoning, however, indicates that real selective activation of the catalyst for one or the other of these two reactions was accomplished.

It has been shown that a decrease in the rate of flow of allyl alcohol increased the percentage of acrolein in the products, as did also an increase in the volume of the catalyst for a constant rate of flow of alcohol. Increasing the activity of a catalyst then should have the same effect as increasing the volume of the catalyst, that is, increasing the activity of the catalyst should increase the percentage of acrolein in the reaction products. The data in the table show that decreasing the rate of alcohol from **50** to **20** cc. per hour (equivalent to increasing the activity of the catalyst) increased the percentage of acrolein from 11.5 to **14.0.** If the effect of these promoters on the catalyst were just the effect produced by an increase in activity, the percentage of acrolein should have increased, but *in* all *cases the percentage of acrolein decreased.* The addition of boric acid to the catalyst lowered the percentage of acrolein from **10.3** to 9.3, and then a decrease in the rate of flow of alcohol to **20** cc. per hour increased the percentage of acrolein back to **10.1.** In a similar manner the chromic acid lowered the percentage of acrolein to **6.3,** but a decrease in the alcohol rate increased the percentage of acrolein to 8.5, and so on for the other promoted catalysts. This shows that the increase in activity of the catalyst due to the promoter was accompanied by an effect opposite to that decreasing the rate of flow of alcohol, instead of the same effect, showing that the real selective activation of the catalyst for one or the other of these two reactions of allyl alcohol had been accomplished.

The nature and extent of modification of the ratio of the simultaneous reactions may be summarized as follows. If the 3A catalyst is used as a standard, boric acid lowered the percentage of acrolein by 1%. Chromic acid lowered it 4%, sodium hydroxide lowered it 2.3% and tungstic acid lowered it 3.8%. Sulfuric acid caused only a slight change in the ratio of the two reactions. The total aldehyde produced was increased by all those substances which lowered the percentage of acrolein. Sulfuric acid lowered the activity decidedly. The boron in the catalyst increased the amount of propionaldehyde produced from **1.40** to **1.57** g. and chromium increased it from 1.40 to **2.33** g., but neither of them changed the amount of acrolein produced (0.16 **g.).** Sodium hydroxide increased the propionaldehyde from 1.40 to 2.53 g. and also increased the acrolein from 0.16 to 0.22 g. Sulfuric acid decreased the propionaldehyde from 1.40 to 1.02 g., and also decreased the acrolein from 0.16 to 0.12 g. Tungstic acid increased the propionaldehyde from 1.40 to 2.90 g., and also increased the acrolein from 0.16 to 0.20 g., being like sodium hydroxide in its action, except that the changes were in different amounts. These results indicate that foreign oxides (assuming the added materials decomposed to give oxides) do effect a selective activation, but the result is specific for the particular oxide, and does not depend on its acidic or basic character.

The alumina catalysts formed by the incorporation of 0.01 mole of boric acid, chromic oxide (F), sodium hydroxide (G) or sulfuric acid (H) with aluminum ethoxide showed a marked lowering in activity for propionaldehyde formation, the figures for similar experimental conditions being as follows: standard Catalyst (D) 1.20 **g.,** (E) 0.56, (F) 0.87, (G) 0.62 and (H) 0.63 g.

Preparation of Catalysts

A. Alumina from hydrated alumina. Hydrated alumina was prepared by adding a very slight excess of ammonium hydroxtde to a dilute solution of aluminum nitrate. The precipitate was allowed to settle and was washed by decantatation three times. Finally it was filtered and dried in an oven at 125° for ten hours. *B.* Crystalline aluminum hydroxide. The product obtained from the Aluminum Company of America, New Kensington, Pa., was washed with water until free from alkali. *C* was alumina from aluminum isopropoxide. This was prepared in a manner similar to *D.* D. Alumina from aluminum ethoxide. Aluminum ethoxide was prepared by the reaction of amalgamated aluminum with dried ethyl alcohol. It had a boiling point of 194.5–203° (uncorr.) (7 mm.). The ethoxide was broken into small lumps and exposed to moist air for two weeks. The powdered material was made into pills as usual. E. Alumina plus boric acid. All of these promoted aluminas were prepared in the same general manner. One hundredth of a mole of the promotor was added to one mole of the fused aluminum ethoxide and the mass was stirred until it solidified. It was then hydrolyzed as in D. F. Alumina plus chromic oxide. Difficulty was encountered in getting all of the chromic acid in solution. This catalyst had a gray-green color, probably from the reduction of the chromium trioxide. G. Alumina plus sodium hydroxide. The aluminum ethoxide was moistened with the correct quantity of an ethyl alcohol solution of sodium hydroxide and then the mass was fused and stirred as in E and hydrolyzed. Sulfuric acid was added in a similar fashion to aluminum ethoxide to give catalyst H.

1A was zinc oxide from zinc oxalate which was obtained by the reaction of zinc carbonate with oxalic acid. One mole of oxalic acid dissolved in 400 cc. of hot water was added slowly to one-half mole of zinc carbonate held in suspension by vigorous stirring in one liter of boiling water. One hour was allowed for the reaction to become complete. The precipitated oxalate was dried, powdered, heated to 130° and dropped into boiling water. These operations were performed three times. Finally the dried oxalate was converted to the oxide by heating it at 400° for one hour. **2A** was zinc oxide from zinc oxalate which was obtained by the reaction of zinc sulfate with oxalic acid. One-half mole of zinc sulfate dissolved in 400 cc of water was added dropwisc to three-quarters of a mole of oxalic acid dissolved in 1000 cc. of water which was stirred vigorously. The precipitated oxalate was washed with cold water until one gram of it dissolved in dilute hydrochloric acid gave no precipitate with barium chloride in one hour. It was dried and heated at 400° for one hour. 3A was a second batch of 1A. 4B was zinc oxide from zinc hydroxide. One-half mole of zinc sulfate dissolved in 400 cc. of water was added dropwise to one and one-half moles of sodium hydroxide dissolved in one liter of cold water which was stirred vigorously. The precipitated hydroxide was washed with cold water, then twice by heating it to 130° and dropping it into boiling water. The final product showed *a* slight test for sulfate. It was converted into zinc oxide by heating it at 400° for one hour, 5B. A second batch of zinc hydroxide prepared according to 4B was divided into two parts, one of which was treated exactly like 4B. This was 5B. 6B. The second portion of the hydroxide in 5B was washed with cold water only, instead of dropping it into hot water. This was 6B. 7B. A third batch of zinc hydroxide was washed only twice with cold water so that it contained considerable sulfate. 8B was zinc oxide prepared by Dr. Paul E. Millington as described under 6B. 9C was zinc oxide (1 mole) plus boric acid (0.01 mole). This catalyst was prepared by covering one mole of zinc oxalate from 1A with a dilute aqueous solution containing 0.01 mole of boric acid and evaporating the whole mass to dryness. This "promoted" oxalate was then heated to convert it into the oxide, just as in the case of 1A. The other promoted oxides were made in a similar manner using appropriate solutes as indicated. Catalysts 9C, 10D, 11E, 12F and 13G were prepared by Dr. Paul E. Millington. 10D was zinc oxide (1 mole) plus chromic acid (0.01 mole). The green color of the catalyst indicated that some of the chromium trioxide was reduced to chromic oxide. 11E was zinc oxide (1 mole) plus sodium hydroxide (0.01 mole); 12F, zinc oxide (1 mole) plus sulfuric acid (0.01 mole); 13G, zinc oxide (1 mole) plus tungstic acid (0.01 mole).

Summary

Allyl alcohol is converted to propionaldehyde over alumina at 330°. This conversion apparently involves an intramolecular rearrangement. This is in contrast to the conversion of allyl alcohol to propionaldehyde over zinc oxide, which depends at least in part upon the reduction of acrolein by a molecule of alcohol.

The activity of alumina for the conversion of allyl alcohol to propionaldehyde was reduced by the addition of 1% boric acid, chromic oxide, sodium hydroxide or sulfuric acid. All except the last of these materials promoted the activity of zinc oxide toward allyl alcohol.

A study has been made of the effect of modifications of zinc oxide catalysts upon the relative amounts of acrolein or propionaldehyde produced from allyl alcohol at 330°.

The source of the zinc oxide determines its selective action toward the two reactions of allyl alcohol. For example, zinc oxide from zinc oxalate gave a higher percentage of acrolein than did zinc oxide from zinc hydroxide. The oxide from zinc oxalate could be reproduced easily, but that from zinc hydroxide could not.

The introduction of acidic or basic substances, such as boric acid, chromic acid, tungstic acid, sulfuric acid and sodium hydroxide, into the zinc oxide caused a selective activation toward one or the other of the two reactions, but the effect seems to be specific for the particular substance and does not depend on its acidic or basic character.

MADISON, WISCONSIN

THE MECHANISM OF THE AZIDE REARRANGEMENT

By Garfield Powell

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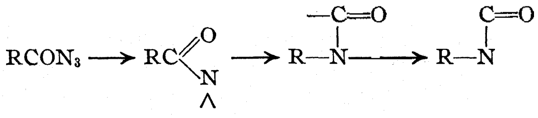
The Beckmann rearrangement and other rearrangements involving the migration of a radical from carbon to nitrogen, including the azide rearrangement to isocyanate, involve a problem of mechanism which is still not solved, though the plausible univalent nitrogen explanation of Stieglitz[1] can be employed as a formulation of the rearrangement in many cases. In the case of the azides the rearrangement involves the univalent nitrogen, thus



Experimental support for the postulate by the examination of the products of decomposition of a di-azide compound has been adduced by Schroeter,[2] and the results are indeed a support of the hypothesis in that they are most simply and directly explained or, rather, represented theoretically, in such a way. There are, however, many possible theories of such mechanisms and the desirable test is one in which the phases postulated in the reaction are shown to exist. In the case of the univalent nitrogen hypothesis the question arises, indeed, as to the possibility of determining the truth of the hypothesis by ordinary chemical means at all. Thus the alkaline reduction of the azides leads to diacyl hydrazines, a reaction well formulated by the univalent nitrogen hypothesis, but not impossible to formulate otherwise. The acid reduction of azides to acid amides is of the same kind. Experiments by the author on the decomposition of azides in a neutral solvent in the presence of triphenylmethyl in the hope of isolating addition compounds of the formula $RCONM_2$ would, if successful, give more valuable support to the hypothesis because of the greater limitation of variables. Benzoyl azide decomposes in benzene solution to give nitrogen and phenyl isocyanate and if the univalent nitrogen phase formed an amide $RCONM_2$ by simple addition in the same solution with a body MM known to be stable in the same solution and not to react with phenyl isocyanate, the number of alternative formulations of the mechanism

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[1] Stieglitz, *Am. Chem. J.*, 18, 751 (1896); This Journal, 25, 289 (1903); etc.

[2] Schroeter, *Ber.*, 42, 2336, 3356 (1909).

would be thereby limited and the postulate gain in plausibility. The highly unsaturated univalent phase would not, in general, be expected to react by addition to other molecules while it is so smoothly capable of saturation by rearrangement but there seems, at first glance, some chance of reaction with bodies such as triphenylmethyl, which has, as conventionally represented, a primary valence capable of direct saturation. However, no reaction takes place and benzoyl azide decomposes in the presence of triphenylmethyl as easily and smoothly as when alone. This, from another point of view, is not unexpected, for whatever intermediary is postulated in the azide rearrangement, it is known to be, in the sense of practice, a saturated one; that is, addenda are not known and it has not been shown to be unusually reactive toward other molecules. Further, it is even stable to the very reactive triphenylmethyl and thus we have a representation of a highly unsaturated substance with one free valence (the unsaturation of triphenylmethyl has been used as an argument in favor of the free radical hypothesis) and its very opposite, in practice, represented with two free valences. There seems to be danger of forming wrong concepts from the simple representation $RCON<$ and it appears to the author that such phases might better be represented in parentheses thus $(RCON<)$, whereby the fact of non-reactivity toward external molecules is evidenced in the formulation. As to the most desirable test, success in the isolation of a simple addition compound would still not be conclusive, for the addition could still be formulated otherwise and the question as to how the compound $RCON_3$ became the compound $RCONM_2$ is one that has, possibly, no relation at all to the question as to how $RCON_3$ became RNCO. It seems that the phase of univalent nitrogen is really a representation of the unobservable dynamic of all reactions and the isolation of any resultants from any reactants leaves the problem still unsolved and still represented in the same way. The next most desirable test, in which the possible alternative formulations are increasingly limited by the chosen conditions of experiment, must therefore be devised, in the present case leading to failure. In the course of the work some new azides and a quinoline hydroximic acid were prepared. Their properties are described below.

Experimental

The decomposition of benzoyl azide into isocyanate and nitrogen was found to be complete in two hours of refluxing in benzene, the isocyanate being recovered as diphenylurea by the addition of aniline and the nitrogen collected and measured by using a current of carbon dioxide into potassium hydroxide to remove the gas. The experiment was repeated, the reaction flask now containing triphenylmethyl, and at the end, after cooling and precipitation of any isocyanate as urea, air was led in to decompose the unchanged triphenylmethyl. The conditions were varied as far as possible and in all cases about 50% of the triphenylmethyl was recovered as peroxide (the usual quantity), nearly all of the isocyanate as urea and no new compounds were recovered. The experiments were persisted in for a long time without success and no evidence of reaction could be obtained by examination of the residues.

Dibenzylacetazide.—In the preparation of acid azides by the interaction of the acid chloride and potassium azide, the employment of a water–acetone mixture was found convenient. Thus the addition of benzoyl azide in acetone to a concentrated solution of potassium azide in water gave, on separation and extraction, an almost theoretical yield of benzoyl azide in a state of purity. Similarly 2,4-dinitrochlorobenzene gave 2,4-dinitro-azidobenzene in purity and good yield, the reaction mixture being kept below 20° and poured into water after shaking. The solid thrown out was collected and recrystallized by dilution of acetone, or otherwise. The melting point is high (67–68°) and the product is colorless, giving on heating on the water-bath dinitrosonitrobenzene as yellow needles melting at TO°. Dibenzylacetazide was prepared in the same way. The reaction mixture was kept below 15° and, after good shaking, thrown into a large excess of water and again shaken until the globules solidified. The solid was collected and washed well with water, dissolved in acetone and water added till cloudy. The crystals were collected, washed with methyl alcohol, and dried in a vacuum desiccator; yield 90%; colorless solid, unstable. When isolated and dried in the desiccator for one hour a melting point (slow) was observed at 51-53'. On standing for one day it becomes completely liquid, gas bubbles arising. The same decomposition into isocyanate takes place on warming or melting.

Dibenzylmethylisocyanate.—A thick liquid, not solidifying in a freezing mixture, it resembles triphenylmethylisocyanate in being only slowly rearranged on heating with water. It is only slightly soluble in alcohol. On refluxing with alcohol in excess for one hour, collecting the solid thrown out when water is added, crystallizing from dilute alcohol and washing with ether, dibenzylmethylethylurethan is obtained, a colorless substance melting at 106–107° (uncorr.). On warming the isocyanate in benzene solution with aniline for a few minutes, and recrystallizing the product from benzene, **dibenzylmethylphenylurea** is obtained as fine silky needles melting at 153–154° (uncorr.). A specimen of the isocyanate was refluxed with water for six hours, the solid formed being occasionally broken up with a rod. Crystallized from benzene, recrystallized from alcohol, *sym.*-di-dibenzylmethylurea was obtained melting at 160–161° as described by Hurd.[3]

2-Phenyl-4-quinolylformhydroximic Acid (Atophane Hydroximic Acid).—The insolubility of the chloride of atophane prevents the formation of the hydroximic acid from the acid chloride and free hydroxylamine. The methyl ester was therefore prepared and the hydroximic acid prepared. Six grams of the methyl ester was dissolved, together with hydroxylamine hydrochloride (1.2 moles) in 50 cc. of methyl alcohol and to the solution was added sodium methylate (2 moles) in methyl alcohol. The mixture was kept just below the boiling point for seven hours and then brought down to small bulk by reduction of pressure, the salt filtered off and an excess of water added. A little of the unchanged ester is thrown out and filtered off. On acidifying, the hydroximic acid is thrown out as a white precipitate; yield, about 80%. It is washed well with water, then with alcohol and benzene successively in small quantities and again with methyl alcohol. Taken up in dilute soda and reprecipitated as before, washed as before, dried at 70° and then *in vacuo*, it analyzes for nitrogen as 10.35%, the calculated

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[3] Hurd, THIS JOURNAL, 43,2242 (1921).

being 10.50% (a gas rush is hard to prevent in the analysis, even after careful grinding of the specimen with fine copper oxide). The compound is very slightly soluble in benzene, more so in ether, most in methyl alcohol and even in this case cannot be said to be more than somewhat soluble in the hot solvent, hydrolysis taking place. It is colorless, melting with gas evolution at 155–156° (uncorr.). It forms a copper salt, drying emerald green and not decomposing under 240°. The silver salt darkens after separation. The benzoyl derivative forms from the sodium salt in water on shaking with an ether solution of benzoyl chloride; it is soluble in methyl alcohol, insoluble in water and melts at 150–151°. It seems to suffer the ordinary decomposition with sodium hydroxide with the formation of an oily and very stable isocyanate.

Summary

A discussion of the azide rearrangement and the possibilities of test of the univalent nitrogen hypothesis is presented. An attempt to arrange an experiment limiting the alternative formulations of the rearrangement is given and the preparation of some azides and a quinoline hydroximic acid is described.

NEW YORK CITY

[CONTRIBUTION NO. 3 FROM THE CHEMICAL RESEARCH LABORATORY OF THE UNITED FRUIT COMPANY]

QUANTITATIVE CHANGES IN THE CHLOROPLAST PIGMENTS IN THE PEEL OF BANANAS DURING RIPENING[1]

BY HARRY VON LOESECKE

RECEIVED NOVEMBER 30, 1928 PUBLISHED AUGUST 7, 1929

Introduction

The purpose of this investigation was to gain some knowledge of the changes which the pigments in banana peel undergo during the process of ripening of the fruit, and the cause of the yellow color. It is a well-known fact that during maturation the fruit changes in color from green to yellow, but no quantitative data seem ever to have been collected indicating the relation of these pigments in the peel of the banana to one another during ripening.

The three pigments estimated were chlorophyll (a + b), xanthophylls and carotin. These are not the only pigments present, as during the process of separation there were indications of flavones and anthocyanins. These latter pigments are present in the cell sap, while chlorophyll, xanthophylls and carotin are present only in the specialized portions of the protoplasm known as plastids.

Method of Investigation

Each determination (Table I) represents the peel from three fingers and these fingers were taken from three separate hands on a specially

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[1] This is one of a series of investigations carried out by the Research Department of the United Fruit Company, to be published in scientific journals.

selected stem.[2] The fruit was of one variety[3] and was ripened under controlled conditions as to temperature and humidity in specially constructed rooms.

The fruit was peeled, the pulp side of the peel scraped free from pulp, the peel cut into small pieces and ground in a mortar with sand. It was practically impossible to macerate green peel fine enough to remove all of the pigment, and even after repeated extractions the peel still showed very faint traces of green. Ripe peel could be mashed to a fine pulp and extraction was apparently complete.

Quantitative determinations of total sugars (calculated as invert sugar) were made on the pulp of the fruit from which the peel was taken.

The peel, prepared as above, was extracted in the cold with 30% aqueous acetone to remove gums and flavones. The chloroplast pigments were then extracted with pure acetone after the method of Schertz.[4] After the chlorophylls had been extracted and saponified to chlorophyllins, they were determined colorimetrically using a solution of chlorophyllins prepared from pure chlorophylls as a standard.

Xanthophylls and carotin, after extraction and separation from the chlorophylls, were determined colorimetrically using a solution of Naphthol Yellow as a standard for the former, and Naphthol Yellow and Orange G as a standard for the latter, after the method of Sprague.[5] It was found impossible to compare xanthophylls and carotin with these dyes by artificial light.

Results

The results of the determinations are given in Table I. The age of the fruit *from the time it* was *discharged from the boat* is given in the first column. In the second column chlorophylls are indicated, in the third xanthophylls, in the fourth carotin and the fifth total yellow pigments (carotin plus xanthophylls). All results are expressed in milligrams of pigment per kilogram of fresh peel.

The sixth column represents percentage of total sugar (as invert) in the pulp of the fruit from which the peel was taken. Prom researches extending over a period of two years during which more than six thousand determinations of total sugar in the pulp of the fruit were made, it has been established that total sugar is the best criterion of the ripeness of the fruit.

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[2] Banana terms are perhaps a little confusing to the uninitiated. A single banana is called a "finger;" the group of fingers, known to the laity as a "bunch," is called a "hand," each containing from 14 to 20 individual "fingers." The cluster of "hands" attached to the stalk is called a "stem."

[3] A variety of *Musa sapientum* known as Gros Michel. This is the yellow variety most common on fruit stands.

[4] Schertz, *Plant Physiology,* 3,211 (1928).

[5] Sprague, *Science,* 67, 167 (1928).

Table I

Chlorophyll, Xanthophyll and Carotin in the Peel or Bananas

Expressed in milligrams per kilo of fresh peel

Days	Chlorophyll (a + b)	Xanthophyll	Carotin	Total yellow pigments	Total sugar (as invert) in pulp, %	Series no.
0	94.5	5.21	1.57	6.78	0.50	
2	15.5	5.45	1.90	7.35	1.64	
3	..	6.31	2.51	8.82	6.14	I
4	00.0	6.57	1.71	8.28	9.92	
0	102.9	7.34	2.05	9.39	0.40	
2	72.5	5.75	1.82	7.57	1.25	
3	48.7	5.91	2.27	8.18	2.24	II
4	29.0	5.70	2.87	8.57	4.54	
5	00.0	3.95	3.56	7.51	11.16	
0	51.7	6.61	1.54	8.15	0.58	
3	40.8	5.09	2.66	7.75	0.81	III
4	14.4	5.41	1.67	7.08	7.63	
0	83.4	5.92	3.66	9.58	0.98	
I	52.5	7.02	2.44	9.46	5.64	IV
0	70.1	7.21	1.22	8.43	0.93	
2	66.1	4.90	3.41	8.31	1.54	
3	14.1	5.15	3.39	8.54	6.52	V
5	00.0	5.00	3.69	8.61	8.25	

The last column, "Series," represents five different groups; in each group there are from two to five determinations depending upon the length of time the fruit was followed during ripening.

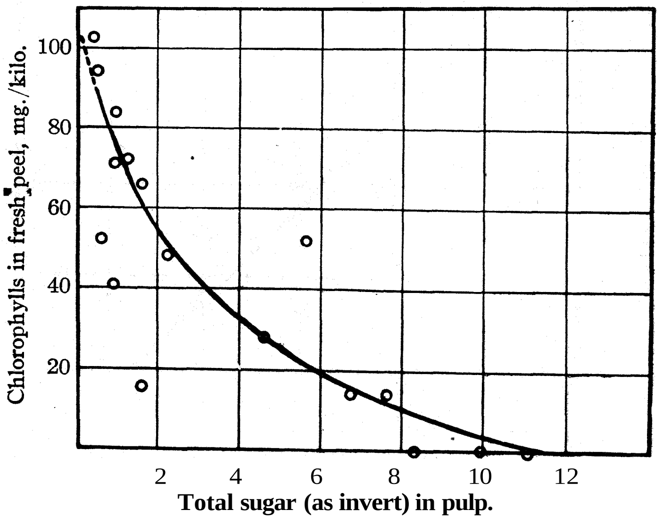

Fig. 1.—Relation of chlorophylls in banana peel to total sugar (as invert) in pulp.

It will be noticed that the total sugar in the pulp varies from 0.4% to nearly 1.0% at zero days (*i. e.*, at time of discharge from the boat). When picked from the tree the fruit contains less than 0.1% of total sugar as invert. Since the chlorophylls in the peel decrease rapidly at first with respect to sugar in the pulp, it follows that the peel of the fruit at the time of harvesting would contain more chlorophylls than at the time of discharge from the boat.

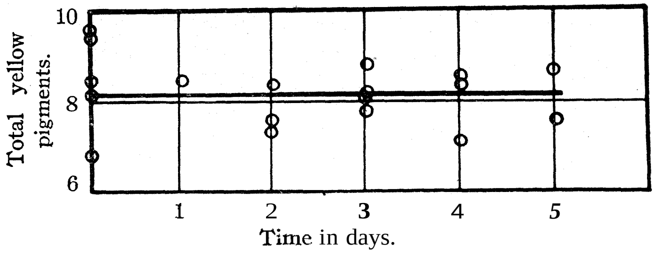

Fig. 2.—Total yellow pigments (xanthophyll and carotin) in banana peel with respect to time.

The amount of xanthophylls is always greater than the amount of carotin and the carotin to xanthophylls ratio changes at various stages during the ripening of the fruit.

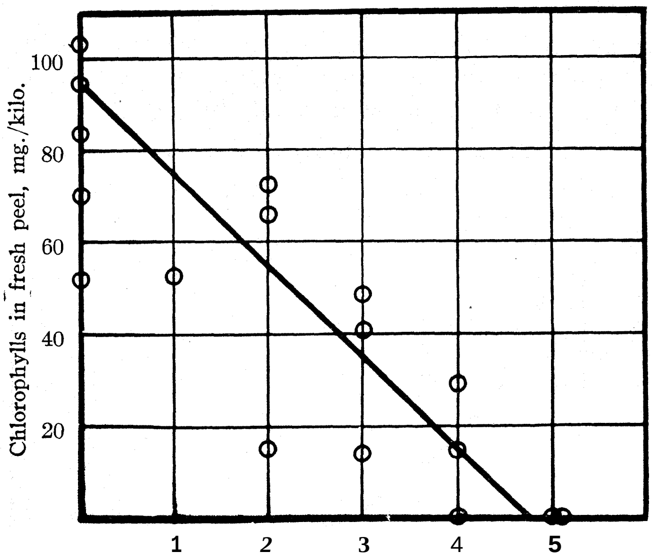

Fig. 3.—Decrease of chlorophylls in the peel of bananas during ripening in respect to time.

The total yellow pigments remain approximately constant throughout the maturation of the fruit (Fig. 2). In other words an unripe banana contains the same amount of total yellow pigments as a ripe banana, but in the case of the former the yellow color is masked by chlorophyll.

Acknowledgment

The writer wishes to express his appreciation to Dr. F. M. Schertz of the Bureau of Soils at Washington, D. C., for his kindness in supplying a sample of pure chlorophyll.

Conclusions

The pigments, chlorophyll (a + b), xanthophylls and carotin were determined in the peel of bananas. Prom the data obtained the following conclusions have been reached: the data indicate that the chlorophyll content of the peel ranges from 102.0 to 51.7 milligrams per kilogram of fresh peel in the unripe fruit at discharge from the boat and decreases as the fruit ripens. Chlorophylls decrease as a straight line function of time (Pig. **3).** The total yellow pigments (xanthophyll plus carotin) remain approximately constant throughout the maturation of the fruit. The amount of xanthophylls is always greater than the amount of carotin, the range of the former being from about 5 to 7 milligrams per kilogram of fresh peel, while the range of the latter is from 1.5 to **3.5** milligrams per kilogram of fresh peel.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE POLARIMETRY SECTION OR THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OP COMMERCE]

THE STRUCTURE OF ALPHA-METHYLXYLOSIDE[1]

BY F. P. PHELPS AND C. B. PURVES

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Crystalline trimethylxylose, derived from the corresponding β-methylglycoside, was the first member of the methylated monosaccharides to which an amylene oxide ring structure could be assigned with certainty,[2] and at the time the opinion was expressed that not only α- and β-methylxyloside, but possibly xylose itself, were similarly constituted. The intervening years, however, have brought to light several cases in which methylating agents, applied to a reducing sugar, have produced derivatives of more than one ring type and, in this connection, the behavior of galactose and arabinose may be cited.[3] Pryde, Hirst and Humphries have shown that in the case of these two sugars methylation with methyl sulfate and alkali undoubtedly gives at least two ring forms. In the case of xylose also this method gives an impure product, the rotation

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[1] **Publication approved by the Director of the Bureau of Standards.**

[2] **Hirst and Purves, J. *Chem. Soc.*, 123, 1352 (1923).**

[3] **Pryde, Hirst and Humphries, *ibid.*, 127, 348 (1925).**

of the methylated products being too low in addition to the yield being small. Our own values using this method are in approximate agreement with those of Carruthers and Hirst,[4] using the same method, and are much lower than the values obtained when pure a- or β-methylxyloside was methylated with silver oxide and methyl iodide. Likewise, it is now well known that the condensation of a reducing sugar with acid methyl alcohol, if carried out at room temperature, yields a γ-methylglycoside, while at higher temperatures such as Fischer used a mixture containing largely the a- and β-forms is obtained. Our own work indicates that all three are formed at an intermediate temperature and that the equilibrium reached in acidified methyl alcohol is not an equilibrium between the a- and β-forms only but between the a-, β-, γ- and perhaps other forms as well, the predominating form being determined by the conditions, temperature playing a particularly important role. As only two of these three forms can have the same ring structure, the third must have a different ring and there is no known way to tell which, if either, of these rings exists in the parent sugar. It accordingly follows that any conclusions regarding the identity of ring structure in the sugar series, to be satisfactory, must be based upon nothing less than a direct experimental identification and correlation of the derivatives concerned. Such a correlation has now been made for a- and for β-methylxyloside.

The earlier methylations of this sugar were carried out by Carruthers and Hirst,[4] who used methyl sulfate and caustic soda to prepare the β-form and who used Fischer's method to condense xylose with methyl alcohol for the a-form. In the latter case after that portion of the β-methylxyloside which crystallized from the product had been removed, the residual crude sirup was treated with silver oxide and methyl iodide and gave a mobile liquid with the elementary composition of a fully methylated pentose. When heated in acid methyl alcohol it displayed a final specific rotation of 50.4°, a value in good agreement with that of 49.5° acquired by trimethyl-β-methylxyloside under similar circumstances. Such behavior has long been known to be characteristic of an α-β pair of methyl glycosides possessing the same ring structure,[5] and the reasonable inference was made that one more example of the same phenomenon had been encountered. While, therefore, it is true that trimethyl-a- and -β-methylxyloside have been correlated, the method used was an indirect one and a series of considerations led the present authors to doubt its reliability in this case. Thus the methylated glycosides examined by the former workers did not conform to the decisive test of similar ring structure devised by Purdie and Irvine[5] in that trimethyl-P-methylxyloside, when hydrolyzed with aqueous acid, yielded a

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[4] Carruthers and Hirst, *J. Chem. Soc.*, 121, 2299 (1922).

[5] Purdie and Irvine, *ibid.*, 104, 9 (1904).

crystalline trimethylxylose, $[\alpha]_D$ 20° in water, while the impure α-isomer gave rise to a levorotatory sirup. Moreover, the correlation adopted by Carruthers and Hirst is pot valid if two trimethylxyloses, differing in ring type, happen to possess similar equilibrium rotations in acid methyl alcohol, a possibility which cannot be counted remote when it is remembered that Haworth and Westgarth[6] have recently prepared a second trimethylxylose with a specific rotation of 31.2" in water, or within 12" of the former figure. Third, in the preparation of trimethyl-β-methylxyloside from xylose by the methyl sulfate and sodium hydroxide, there is some uncertainty because of the small yield obtained, together with the suspicion that this method does not always yield a single product. If the trimethyl-8-methylxyloside contained a large unknown percentage of a second compound of similar properties and therefore difficult to separate and, as in this case, on hydrolysis yielded less than 50% of the theoretical amount of trimethylxylose, it would be difficult to say which of the two components in the parent mixture produced the trimethylxylose. A fourth consideration lay in the fact that a-methylglucoside, galactoside and arabinoside are directly correlated, in each case, to methylated derivatives which very probably possess an amylene oxide ring.' It follows that a similar structure must be assigned to the glycosides themselves and, if this is so, a computation in molecular rotations by the method of Hudson[S] leads to the conclusion that the 1:5 oxygen linking is not present in a-methylxyloside. As this is at variance with the accepted structure for the β-isomer, Dr. C. S. Hudson requested us to repeat the work of Carruthers and Hirst and to obtain more decisive experimental evidence on the matter.

The carefully purified crystalline a-methylxyloside was methylated by the silver oxide reaction and every care was taken to render the methylation complete. Although the trimethyl-a-methylxyloside could not be made to crystallize and purification was carried out by the uncertain method of distillation, the specific rotations determined, 121.7° in chloroform, 112.7° in water and 122° in methyl alcohol, are regarded as approximately correct. When methylated in similar fashion β-methylxyloside gave an excellent yield of the crystalline, fully methylated derivative. Purification was rigorous and the final constants were: m. p. 51°; $[\alpha]_D^{20}$ —69.5" in chloroform and —81.7" in water. Aqueous acid, of a lower concentration and at a lower temperature than that previously employed, hydrolyzed both trimethylmethylxylosides, 80–85% of the theoretical yield of crystalline trimethylxylose being isolated in each case. The two

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[6] Haworth and Westgarth, J. Chem. *Soc.*, 129,880 (1926).

[7] Charlton, Haworth and Peat, *ibid.*, 129, 89 (1926); Hirst, *ibid.*, 129, 350 (1926); Hirst and Robertson, *ibid.*, 127, 358 (1925); Haworth, Ruell and Westgarth, *ibid.*, 125, 2468 (1924).

[8] Hudson, THIS JOURNAL, 48,1434 (1926).

specimens of the sugar were then compared with each other and found to be identical. Mutarotation in water was swift, the initial specific rotation being 65° and the equilibrium rotation 17.7" in place of the value of 20° hitherto accepted as standard. Trimethylxylose occasionally displayed mutarotation in chloroform solution, the initial value of $[\alpha]_D^{20}$ 58" diminishing to 24°; also, the initial rotation to this solvent was quite erratic, lying anywhere between 58 and 45° after recrystallization from ether solution. In these cases it is possible that the sugar crystallized as a mixture of the a- and β-forms. The value of 58° is therefore to be taken with caution. One other point remained to be considered, for trimethyl-β-methylxyloside prepared by the methylation of xylose in alkaline solution had a specific rotation some 10° lower than the correct value of —69.5' in chloroform. The similar observation of Carruthers and Hirst was thus confirmed and, recrystallization failing to improve the constant, the possibility remained that the two methods of alkylation had produced isomeric substances. On hydrolysis, however, the specimen with the incorrect specific rotation also gave trimethylxylose in 75% of the theoretical amount and the discrepancy was seen to be due to an impurity, possibly an isomeric form, which was difficult to remove. This observation should be of value when it is desired to prepare a methylated sugar in a state of optical purity by the aid of methyl sulfate and of alkali.

Experimental[9]

Preparation of Trimethyl-β-methylxyloside.—(a) A 5-g. portion of pure crystalline β-methylxyloside, $[\alpha]_D^{20}$ —65" in water, was methylated in the standard fashion with 40 g. of silver oxide and 25 cc. of methyl iodide, a little methyl alcohol being present in this first methylation only to dissolve the glucoside. Acetone was used to recover the product, which was then submitted to a second and a third treatment with the same reagents. The final separation of the trimethyl-β-methylxyloside from the inorganic residues was effected by extraction with ether, the yield of the crude, crystalline material after evaporation of the ether being 5.52 g, or 88% of the theoretical. After three recrystallizations from petroleum ether, cooled in ice and salt, the specific rotation in purified chloroform was $[\alpha]_D^{20}$ —69.6' (0.2439 g. in 25 cc. of $CHCl_3$ rotated the plane of polarization 1.36" to the left in a 2-dm. tube). This value was not appreciably changed by two further recrystallizations, the value found being $[\alpha]_D^{20}$ in $CHCl_3$, —69.5" (0.3669 g. in 25 cc. gave a rotation of —2.04° in a 2-dm. tube). The average of four sets of readings by two observers was $[\alpha]_D^{20}$ in $CHCl_3$, —69.5'. The rotation in water was $[\alpha]_D^{20}$ —81.7' (0.2463 g. in 25 cc. read —1.62" in a 2-dm. tube). The substance melted sharply at 51°. Estimation of methoxyl by Zeisel's method: 0.3144 g. gave 1.3968 g. of silver iodide, corresponding to 58.7% of OCH_3; calcd., 60.2. A subsequent

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[9] All methylations with silver oxide and methyl iodide were carried out in a round-bottomed flask equipped with an efficient water-cooled condenser, the two being united by a ground-glass joint in place of the customary rubber stopper. This innovation, while giving a product free from contamination by rubber and therefore more readily purified, required care in its use, as flask and condenser readily became cemented together.

larger-scale preparation (23 g.) after purification by several recrystallizations from ordinary absolute ether cooled in ice yielded substantially the same figures for the specific rotation, namely, −69.4° in $CHCl_3$ and −81.8" in H_2O.

(b) A 25-g. sample of carefully purified xylose was methylated as described by Carruthers and Hirst[4] first with methyl sulfate and alkali and then with 33 g. of silver oxide and 17 cc. of methyl iodide. The product crystallized on recovery from the latter process; yield, 20 g. or 64% of the theoretical. Once recrystallized from petroleum ether, 0.0684 g. dissolved in 25 cc. of chloroform and in a 2-dm. tube had an observed rotation of −0.34' and a specific rotation of −59.6". A second recrystallization failed to change this value (0.1268 g. in 25 cc. of the same solvent had α −0.60° and $[\alpha]_D$ −59.0"). It is to be noted that the yield was only 64% as against 88% in (a), and likewise that the rotation is about 10° lower.

Preparation of **Trimethyl-α-methylxyloside.**—(c) Pure a-methplxyloside, prepared by the method of Bourquelot,[10] $[\alpha]_D$ +154.0° in water, was methylated with 60 g. of silver oxide and 37.5 cc. of methyl iodide for a 7.5-g. sample. Methyl alcohol (2.5 cc.) was also present, in this first methylation, to enable the xyloside to dissolve. Three such operations, however, failed to complete the methylation, as was evident when the liquid product was distilled, the refractive index varying with the fraction on which it was observed: methoxyl, found, 58.4%; theoretical, 60.2%. Accordingly, the total distillate of 7 g. was remethylated with 8 g. of silver oxide and 5 cc. of methyl iodide. After recovery it was dissolved in water and extracted with chloroform in order to remove most of the lower methylated impurities and the sirup obtained from the anhydrous chloroform extract was methylated for a fifth time. Evaporation at 80° (20 mm.) freed the trimethylmethylxyloside from solvent, the last traces of which were eliminated during the distillation, bath 110" (10 mm.). Rejecting the first six drops of the distillate, the seventh was found to have n_D^{24} 1.4391 and the last n_D^{25} 1.4387. Since data drawn from the work of Carruthers and Hirst show that the change in refractive index per degree rise in temperature is −0.00036" for a methylated xylose, the indices quoted are regarded as equivalent. In an estimation of methoxyl groups by Zeisel's method, 0.11.51 g. gave 0.5208 g. of silver iodide; found: OCH_3, 59.7; calcd., OCH_3, 60.2.

In purified chloroform, $[\alpha]_D^{20}$ was +121.2°, 0.7273 g. having an observed rotation of 7.06" in 25 cc. of solution and in water +112.2°, values not appreciably changed by redistillation. After one redistillation $n_D^{22\ 8}$ of the fifteenth drop was 1.4398, that of the last, at 23°, 1.4397, while 0.4710 g. in 25 cc. of chloroform solution had a, 4.59" and $[\alpha]_D^{20}$ +121.7°. Trimethyl-a-methylxyloside, therefore, has a specific rotation in chloroform of the order of +121.5°. Similar measurements were made in water and in methyl alcohol; $[\alpha]_D^{20}$ in water was +112.7° (0.2942 g. in 25 cc. gave a rotation of 8.61° in a 2-dm. tube); $[\alpha]_D^{19}$ in CH_3OH was +122.2° (0.3791 g. in 25 cc. gave a rotation of +3.70° in a 2-dm. tube).

Preparation of **Trimethyl-α-xylose.**—(a) Pure trimethyl-β-methylxyloside, 6.29 g., dissolved in 120 cc. of 4% hydrochloric acid, was maintained at a temperature of 85°. The initial specific rotation of −73.1° increased, during seventy-five minutes, to a nearly constant value of +14.8°, whereupon the solution was neutralized with barium carbonate and filtered. In this preparation, trimethylxylose was isolated by a tedious extraction of the filtrate with large volumes of chloroform and by evaporation of the anhydrous extract to a sirup. A partial crystallization quickly occurred and the crystals were recrystallized from ice-cold ethyl acetate; yield, 2.3 g.; m. p. 91–92"; $[\alpha]_D$ f-54.3" in chloroform. The original mother liquors, on standing at 0° for two days, deposited a further 1.2 g.; m. p. 88–91°; $[\alpha]_D$ +53.8° in chloroform, while further quantities

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[10] Bourquelot, *Ann. chim.*, 3,298 (1915).

were obtained from the residual sirup on longer standing. Eventually the yield of crystalline trimethylxylose reached **85%** of the theoretical. After two recrystallizations from ether, **0.5309** g. in **25** cc. of the chloroform solution had a rotation of **2.40'** or $[\alpha]_D$ +56.4°. The third and fourth crystallizations raised this figure to $[\alpha]_D$ +58.0° **(0.3223** g. **in 25** cc. of chloroform had $\alpha = 1.50°$), a value which was not obtained when climatic conditions were hotter and more humid.

Mutarotation in **Water.--0.2988** g. dissolved in **25.10** cc. had $\alpha =$ **0.55'** twenty minutes after solution, while the equilibrium rotation of +0.43° was reached in three hours. The corresponding specific rotations are $[\alpha]_D$ **4-23°** and $[\alpha]_D$ **+17.9°**, respectively.

(b) Recrystallized **trimethyl-β-methylxyloside,** $[\alpha]_D$ in $CHCl_3$ −59.6°, prepared by the direct methylation of xylose by methyl sulfate and alkali, was hydrolyzed under conditions similar to those detailed above. The specific rotation of the solution became practically constant at +16.2° and as this corresponds to an almost quantitative yield of trimethylxylose, the acid was neutralized with an excess of lead carbonate. Filtration removed the greater part of the inorganic salts from the well-cooled liquor and evaporation of the filtrate under diminished pressure left a dry residue from which hot ether readily extracted trimethylxylose. The sirupy product crystallized in stages when kept in the ice box for ten days, the final yield of crystalline material being 75% of the theoretical. Recrystallized from ether, the melting point was 90° and the mixed melting point with the specimen from (a) was **91–92'.** Mutarotation occurred in chloroform, **0.4477** g. of the trimethylxylose in **25** *cc.* of solvent gave a reading of $\alpha =$ **1.99'** or $[\alpha]^{20}_D$ +55.8°, falling in ninety minutes to the constant value $\alpha =$ **0.86"** or $[\alpha]^{20}_D$ +24.2°, not changed by catalysis with a trace of acid. In water the first observation was made one minute after solution, **0.2392** g. in **25** cc. having **a** = 1.16°, decreasing to the constant value of a = **0.34'** in one hour. The corresponding specific rotations were $[\alpha]^{20}_D$ +62.8° and final $[\alpha]^{20}_D$ +17.6°.

(c) **Liquid trimethyl-a-methylxyloside (2.48** g.) was dissolved in **4%** hydrochloric acid and the volume increased to **50** cc. by addition of the same reagent. When maintained at **85'** the specific rotation of the solution decreased from +109° to +19.4° in the course of **270** minutes. The yield of trimethylxylose, isolated **as** in (b), was **80%** of that theoretically possible; m. p. **91–92';** mixed melting point with the two specimens obtained above, **91–92"** in each case.

Mutarotation in Water.--0.2810 g. in **25** cc. of aqueous solution was read in **a 2-dm.** tube at **22°.**

Minutes	0.5	2	3	4	5	8	13
$[\alpha]^{20}_D$	62.1	57.4	55.2	52.4	50.8	43.9	35.5
Minutes	21	24	34	48	88	123	180
$[\alpha]^{20}_D$	28.4	27.1	22.8	19.4	18.5	17.7	17.7

Extrapolation from these data gave a value of +64° for the initial specific rotation of trimethyl-a-xylose in water, while in a duplicate experiment **$65'** was the figure obtained.

The authors record their warm appreciation of the interest Dr. C. S. Hudson has **taken** in the work. One of them (C. B. P.) also wishes to thank the Commonwealth **Fund** of **New** York for the Fellowship which made his collaboration possible.

Summary

Trimethyl-a-methylxyloside has been prepared from pure crystalline a-methylxyloside. After purification by distillation its constants were n^{23}_D, **1.4397;** $[\alpha]^{20}_D$ **in** $CHCl_3$, **+121.5°;** $[\alpha]^{20}_D$ **in** H_2O, **+112.7;** $[\alpha]^{20}_D$ in CH_3OH, **+122.2.**

Trimethyl-β-methylxyloside has been prepared in two ways: (a) from pure crystalline β-methylxyloside and (b) from pure xylose, using the methyl sulfate and sodium hydroxide method. After purification by recrystallization, *the* crystals resulting from (a) had the following constants: m. p. sharp at 51°; $[\alpha]^{20}_{D}$ in $CHCl_3$, –69.5"; $[\alpha]^{20}_{D}$ in H_2O, –81.7, while those resulting from (b) showed $[\alpha]^{20}_{D}$ in $CHCl_3$, –59.6°. As this value, which is about 10° low, did not change appreciably on recrystallization, it is concluded that this method gives a less pure product. *So* hydrolysis both trimethyl-a-methylxyloside and trimethyl-β-methylxyloside yield the same crystalline trimethylxylose. It is therefore concluded that these two substances contain the same ring structure, forming an α- and P-pair. They have thus been definitely correlated for the first time and likewise the parent substances, **a**- and β-methylxylosides, from which they were derived. The properties of the purified trimethyl-α-xylose were m. p. 91 to 92°; $[\alpha]^{20}_{D}$ in $CHCl_3$ (final), + 24.2; $[\alpha]^{20}_{D}$ in H_2O (initial), 64.5°; (final), 17.7°. It is to be noted that for the most part the constants given above differ quite materially from those previously recorded.

WASHINGTON, D. C.

[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PROMOTER ACTION WITH OXIDE CATALYSTS FOR THE DECOMPOSITION OF ALCOHOLS[1]

BY HOMER ADKINS AND PAUL E. MILLINGTON

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It has been shown by experimental work described in a series of papers from this Laboratory[2] that the ratio of reaction products formed when alcohols are passed over solid catalysts is not primarily a function of the chemical nature of the catalyst mass but is determined by easily modifiable characteristics of the catalyst surface. Two explanations have been offered for this variation in the ratio of reaction products. Hugh Stott Taylor[3] in an extended discussion of our results among others stated that the oxides are dual catalysts, the metal part (metal ion) being dehydrogenating, and the oxygen part (oxide ions) being dehydrating. The ratio of the simultaneous reactions would then depend in part upon the ratio at the surface of active metal ions and active oxide ions. This latter ratio would depend upon the original distribution and upon the

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[1] The authors are indebted to E. I. du Pont de Nemours and Company for a fellowship held by Dr. Millington during the academic year 1927–1928.

[2] For references see Adkins and Lazier, THIS JOURNAL, 48, 1671 (1926).

[3] Taylor, "Colloid Symposium Monograph," The Chemical Catalog Company. Inc., New York City, 1926, Vol. IV, p. 25.

relative extent to which the two kinds of ions had been covered up by poisons. Upon the basis of this hypothesis the selective activation of catalysts observed in this Laboratory was dependent upon the relative occurrence in the catalyst surface of the two kinds of ions and upon selective poisoning of the one or the other kind of ions. Taylor further says that "the prediction can, therefore, be freely made that the presence of sulfate ion, and, for similar reasons, the anions of all the oxyacids, will cause an increase in dehydration ratio in the case of such predominantly dehydrogenating catalysts as uranium oxide, molybdenum oxide, ferric oxide and vanadium oxide." The adsorption of alkali ions will, on the contrary, favor dehydrogenation.

Adkins had previously suggested that the variation in the ratio of simultaneous reactions, was in part, a function of the space relationships of the active centers of the catalysts, i. e., that the direction of distortion of an adsorbed molecule would be determined by the chemical nature of the catalyst and also by the relative position in space of the adsorbing centers which are close enough together to exert their influence simultaneously upon a single adsorbed molecule. Differences in spacings of the centers of activity might produce different molecular fragments just as the size and shape of fragments of a piece of paper would be in part determined by the relationship in space of the two hands which tore the original sheet. On the basis of this hypothesis small amounts of added materials might modify the ratio of reaction products through their effect in disturbing the spacial relations of the active centers on the catalyst surface. Such effects would presumably be highly specific and unconnected with the acidity or alkalinity of the added material and would vary from alcohol to alcohol, as a spacing favorable for a high dehydrogenation ratio of one alcohol would not be likely to be favorable for all alcohols.

A criticism of these hypotheses necessitates that there be available very accurate data over considerable intervals of catalyst life on the ratio of reaction products over a variety of pure and promoted catalysts. The experimental work described in this paper was carried out in order to provide such data.

Apparatus and Method of Experimentation

The assembly of the apparatus used for this work is indicated in Fig. 1. The catalyst tube was of pyrex, of which the upper half, eighteen inches in length, was constructed of quarter-inch tubing and carried the male half of the ground-glass joint. The lower half was of half-inch tubing, fourteen inches in length. A Gooch filter plate was pressed against a slight constriction in the tube at a point which fell near the center of the furnace when the apparatus was assembled. The tube was indented for the entire length above the filter plate.

A fine capillary, drawn out at one end of a piece of ordinary capillary tubing, was connected by a section of rubber tubing to the female half of the ground-glass joint mentioned in the preceding paragraph, in such a way that the tip of the capillary extended well down into the wide part of the joint. Alcohol or other liquid, contained in a liter bottle, was forced through the capillary by means of compressed air, maintained at practically a constant pressure by a column of water confined in a rubber tube leading from a reservoir in an upper room to a storage bottle on the laboratory desk. This bottle carried a simple manometer and was connected through a sulfuric acid drying tower with the flask containing the alcohol. The lower part of the catalyst tube carried a rubber stopper over which was fitted a glass cup with an outlet for gases and condensed liquid. A small pyrex tube also projected through the cup, the tip of the tube pressing against the catalyst. Ordinarily this tube served only to hold the catalyst mass in place. If the temperature of the reaction was wanted, a thermocouple was inserted into the tube and the tip of the latter imbedded in the catalyst. Another potentiometer was connected to the thermocouple and the temperature read off as desired.

The liquid was vaporized in the upper part of the catalyst tube by means of a preheating device. This consisted merely of a fourteen-inch length of pyrex tubing wound with eighteen feet of No. 18 nichrome wire and covered with asbestos. A current of two amperes maintained a temperature of 170 to 180". A multiple unit furnace was used to heat the catalyst tube. It was maintained at the desired temperature, plus or minus three degrees, by a Leeds and Northrup controller through the medium of a thermocouple mounted on the tube close to the catalyst mass.

Two forms of sampling apparatus were used. The first consisted of a 300-cc. calibrated bottle filled with saturated sodium bromide solution and fitted with a three-way stopcock. A second bottle served as a reservoir for the salt solution as it was displaced from the first bottle by the incoming gases. The second form provided for the condensation of the vapors issuing from the catalyst tube. The condensing system consisted of a 200-cc. round-bottomed flask fitted with a short glass coil, which served as the inlet, and a small upright coil condenser. The whole was-immersed in an ice-bath and the uncondensed gases were collected over saturated sodium bromide solution in a calibrated three-liter bottle.

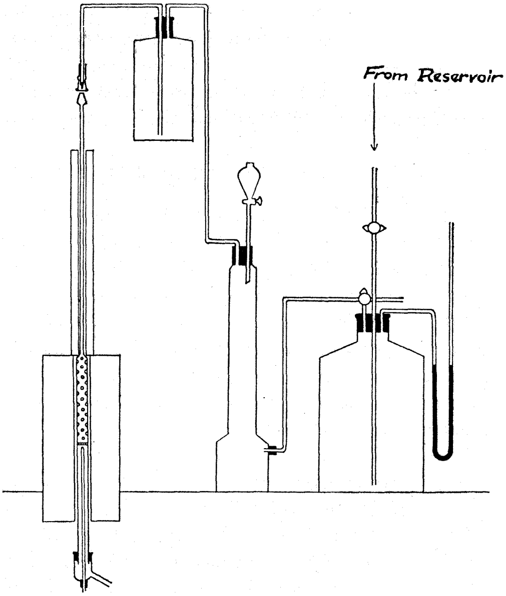

Fig. 1.—Apparatus for gas phase catalytic reactions.

The charge of the catalyst, consisting of quartered tablets 6 mm. in diameter, was placed against the Gooch filter plate and held in place by a wad of glass wool. Air, partially dried and purified by bubbling through sulfuric acid, was slowly passed over the catalyst for fifteen minutes at the temperature maintained for the succeeding reaction.

Samples of gas were ordinarily taken at atmospheric pressure in the 300-cc. bottles. The contents of the sampling bottle were well shaken to dissolve aldehyde and alcohol vapors, and to displace gaseous products from the condensate layer. When the condensate was extremely insoluble in the salt solution, this method was unreliable due to the comparatively large amounts of unsaturated hydrocarbons remaining dissolved in the condensate layer. In such a case the gases were first passed through the condensing system described above and collected in the calibrated three-liter bottle for a definite period. The condensing system was removed from the ice-bath without being disconnected from the gas holder, and the condensate refluxed under the short coil condenser until no more gas was evolved. The condensing coil, flask and reflux condenser were finally filled with boiling water to displace all of the gas they contained.

Gas Analysis.—The procedure used in determining the percentages of the constituents of the evolved gases was essentially that of Hempel. Samples were measured in a 100-cc. water-jacketed buret over water. Carbon dioxide, uncondensed acid and alcohol vapors were absorbed in 40% potassium hydroxide solution. Unsaturated hydrocarbons were removed by bromine water, oxygen by stick phosphorus and carbon monoxide by ammoniacal cuprous chloride. Hydrogen and methane were determined by combustion. When ethane was also present, hydrogen was absorbed in colloidal palladium[4] and the residue burned in an excess of oxygen.

Preparation of Catalysts

No. 1. Millington's zinc oxide *ex* sulfate was prepared by adding a 0.67 N solution of zinc sulfate dropwise to a well-stirred 0.67 N hot solution of sodium hydroxide. The precipitate was washed repeatedly with hot water and finally dried at 120° for twelve hours. There were traces of sulfate in the catalyst.

No. 2. Weston's zinc oxide *ex* sulfate was prepared by adding 0.5 mole of zinc sulfate dissolved in 400 cc. of water dropwise with rapid stirring to 1.5 moles of sodium hydroxide in a liter of cold water. The precipitate was washed twice with cold water, then twice by heating to 130° and dropping into boiling water. Traces of sulfate remained in the catalyst.

No. 3. Lazier's zinc oxide *ex* sulfate was prepared but was not used during the investigation reported on in 1926. The sodium hydroxide solution had been added to the zinc sulfate solution. The catalyst contained considerable sulfate.

No. 4. Lazier's zinc oxide *ex* sulfate "A" was the catalyst described under that symbol in 1926. It was prepared in the same way as No. 3.

No. 5. Zinc oxide *ex* acetate was made from the acetate; otherwise the procedure was the same as for No. 1.

No. 6. Zinc oxide *ex* zinc chloride was made similarly to No. 1.

No. 7. Zinc oxide *ex* zinc nitrate was made similarly to No. 1.

No. 8. Zinc oxide *ex* oxalate was prepared from zinc oxalate by heating to 400° for forty-five minutes. The oxalate was prepared by slowly adding a hot solution of 1.4 moles of oxalic acid in a liter of water to a vigorously stirred suspension or solution of 1.0 mole of commercial zinc oxide, zinc carbonate or zinc chloride. The mixture was then boiled for 0.5 hour, filtered and the oxalate washed several times with hot water, dried, powdered, heated to 130°, poured into boiling water, filtered and dried at various temperatures from 90 to 120°. The oxalate showed no test for sulfates or chlorides.

No. 9. Zinc oxide *ex* oxalate and chromic oxide was prepared by treating 50 cc. of a water suspension of 17.7 g. of zinc oxalate with 0.2 g. of chromic oxide. The mixture was heated to dryness and decomposed for forty-five minutes at 400° as in the case of No. 8; 0.01 mole of chromic oxide was calculated to be present for each mole of ZnO.

No. 10. Zinc oxide *ex* oxalate + B_2O_3 was the same as No. 9 except that 0.124 g. of boric acid replaced the chromic oxide; 0.01 mole of B_2O_3 per mole of ZnO.

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[4] Paal and Hartmann, *Ber.*, 43, 243 (1910).

No. 11. Zinc oxide *ex* oxalate + WO_3 was the same as No. 9 except that 0.25 g. of commercial H_2WO_4 replaced the chromic oxide; 0.01 mole of WO_3 per mole of ZnO.

No. 12. Zinc oxide *ex* oxalate + V_2O_5 was prepared by grinding 0.182 g. of vanadium pentoxide with 17.7 g. of zinc oxalate and then heating to 400° as usual.

No. 13. Zinc oxide *ex* oxalate + ammonium vanadate was prepared similarly to No. 9 except that 0,234 g. of ammonium metavanadate, NH_4VO_3, was used instead of the chromic oxide.

No. 14. Zinc oxide *ex* oxalate + MoO_3 was prepared the same as No. 9 except that 0.18 g. of ammonium molybdate was used.

No. 15 Zinc oxide *ex* oxalate + H_2SO_4 was prepared by evaporating to dryness and heating to 400° a mixture of 18.9 g. of hydrated zinc oxalate and 19.5 cc. of 0.1024 *N* sulfuric acid.

No. 16. Zinc oxide *ex* oxalate + NaOH was prepared the same as No. 15 except that 5 cc. of 0.2 *N* sodium hydroxide replaced the sulfuric acid.

No. 17. Iron oxide *ex* ferrous oxalate was prepared by heating ferrous oxalate for one hour at 400°. The oxalate was prepared by precipitation from solutions of ferrous sulfate and oxalic acid.

No. 18. Iron oxide *ex* ferrous oxalate + H_2SO_4 was prepared in the same way as No. 15 except that ferrous oxalate replaced the zinc oxalate.

No. 19. Iron oxide *ex* ferrous oxalate + NaOH was prepared similarly to No. 16.

No. 20. Iron oxide *ex* ferrous oxalate + B_2O_3 was prepared similarly to Nos. 9 and 10.

No. 21. Ferrous oxalate *ex* oxalate + CrO_3 was prepared similarly to No. 9.

No. 22. Titania *ex* tetra-butyl orthotitanate was prepared by allowing tetra-butyl orthotitanate to hydrolyze over water at 50 to 60° in a partially evacuated desiccator.

No. 23. Titania *ex* tetra-ethyl orthotitanate was prepared similarly to No. 22.

No. 24. Titania as in No. 23 + B_2O_3 was prepared by adding 20 cc. of an alcoholic solution containing 0.062 g. of boric acid to 4.0 g. of titania and then evaporating the alcohol during stirring.

No. 25. Titania from the hydrolysis of a mixture of tetra-ethyl titanate and sodium hydroxide was prepared by allowing a mixture of 50 parts of tetra-ethyl orthotitanate and 1 part of sodium hydroxide to hydrolyze as in No. 22.

No. 26. Titania *ex* tetra-ethyl titanate + NaOH was prepared similarly to No. 24

No. 27. Alumina *ex* aluminum butoxide was prepared similarly to No. 22 except that the partially hydrolyzed material was heated to 80 to 90° from time to time during the hydrolysis.

No. 28. Alumina *ex* aluminum butoxidc + CrO_3 was prepared by the hydrolysis of a mixture of chromic oxide and aluminum butoxide.

No. 29. Alumina *ex* aluminum butoxide + sodium hydroxide was obtained similarly by allowing a butanol solution of the butoxide and sodium hydroxide to hydrolyze.

No. 30. Alumina *ex* aluminum butoxide + H_2SO_4 was obtained by passing sulfur trioxide into aluminum butoxide and then allowing the mixture to hydrolyze.

At least two preparations of each catalyst were made and used except for some of the promoted iron and aluminum catalysts. For all catalysts which are claimed to be reproducible the gas analyses in the reaction products agreed within less than 1%. The promoted catalysts are qualitatively but not quantitatively reproducible; that is to say, chromium-promoted catalysts were always found to be more efficient for dehydration than were boron-promoted catalysts although the exact figures would vary somewhat. The data plotted in Figs. 2 and 3 are the results of two or more runs made on different samples of the same preparation of a catalyst. The points on the curve represent actual experimental determinations and are not averages. It is believed that differences in percentage of gases which are greater than 0.4% are significant of actual differences between the catalysts concerned. In the case of zinc oxide catalysts, from 0.0 to 2.5% of carbon dioxide was found to be present in the gases of reaction. This has been calculated out of the results and the alkene and hydrogen calculated as though they constituted 100% of the gas. There seems to be no adequate explanation of the variation in the formation of carbon dioxide over zinc oxide catalysts. Catalysts usually decrease on standing with respect to the formation of carbon dioxide. Therefore there seems to be some easily modified characteristic of the catalyst surface which determines the formation of carbon dioxide.

Summary of Experimental Results

A study of the effect of promoters demands the selection of a standard catalyst which can be readily reproduced and which is not modified in activity by the operations necessary for the incorporation with it of the promoter. Precipitated zinc oxide is not such a catalyst, as may he seen from the data given in Fig. 2 for the behavior of ethanol over a number of precipitated zinc oxides.

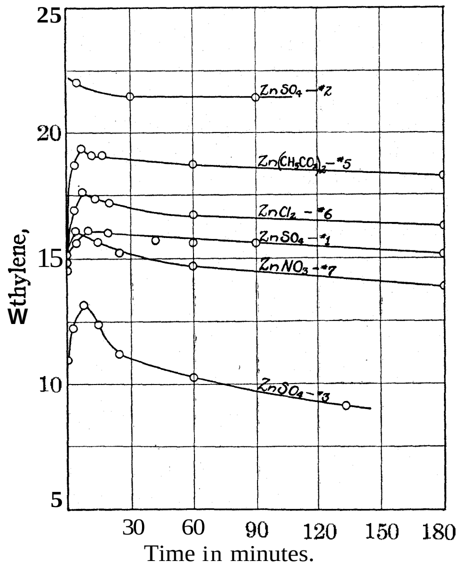

Fig. 2.—Percentage of ethylene in gaseous products from ethanol over various-precipitated zinc oxide catalysts.

Zinc oxide obtained by the ignition of zinc oxalate seemed to be an excellent standard catalyst. Several different preparations from zinc oxide and oxalic acid, from zinc chloride and oxalic acid, and from basic zinc carbonate and oxalic acid gave practically identical ratios of ethylene and hydrogen. The percentages of ethylene in two typical experiments are given below: 5 min., 25.7 and 25.8%; 20 min., 24.7 and 25.0%; 45 min., 24.0 and 24.3%; 90 min., 23.2 and 23.6%; 120 min., 23.3 and 23.7%. It is not feasible to incorporate promoters with zinc oxide through the use of water solutions because this treatment in itself modifies the ratio of dehydrogenation and dehydration shown by the catalysts. However, alcoholic solutions may be used for the addition to and removal of alcohol from zinc oxide without modifying its catalytic effects. Promoters may be incorporated with zinc oxalate through the use of aqueous solutions or suspensions.

The effect upon the ratio of dehydration to dehydrogenation of ethanol of adding small amounts of various materials to zinc oxide ex oxalate is shown in Fig. 3. The effect of some of these same promoters upon the ratio of gaseous products from ethanol over titania is shown in Table II. The percentage of alkene formed from ethyl, *n*-propyl, *iso*propyl and *iso*butyl alcohols over nine different zinc oxide catalysts is shown in Table III. The percentage of hydrogen present in the gaseous products equals the difference between 100 and the percentage of alkene shown in the table for a given set of conditions. The data obtained in the use of the alumina catalysts are not given in a table because all of them except the one containing sodium oxide gave a gas containing 98 to 99% ethylene after the removal of alkali-soluble materials amounting to about 5%. The sodium oxide aluminum catalysts had a very low activity and showed about nine parts of ethylene for one part of hydrogen. This effect of sodium oxide in lowering activity and producing hydrogen is characteristic. The volume of hydrogen produced is small and is in all probability due in part to the catalytic action of sodium oxide as distinguished from its promoter action.

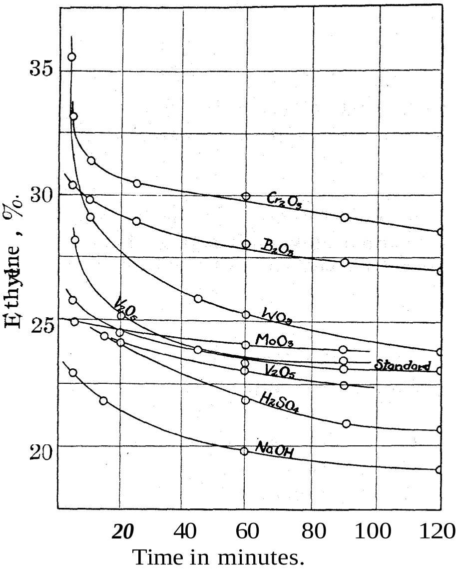

Fig. 3.—Percentage of ethylene from ethanol over "promoted" zinc oxide catalysts.

TABLE I

ETHANOL OVER IRON OXIDE CATALYSTS

Samples taken after 0.5 g. of catalyst had been used for one hour at 400°; rate of alcohol flow, 50 cc. per hour.

No.	Catalyst	CO_2, %	CO, %	C_2H_4, %	C_2H_6, %	H_2, %
17	Standard ex ferrous oxalate	10.2	1.1 to 1.7	6.1	7.5	76.2
18	Standard + H_2SO_4	4.8	1.1 to 1.7	7.0	7.5	80.8
19	Standard + NaOH	5.0	4.7	1.1	1.3	87.8
20	Standard + B_2O_3	6.2	1.1 to 1.7	10.8	18.9	64.0
21	Standard + CrO_3	8.4	1.1 to 1.7	7.1	8.8	75.6

A consideration of the data contained in the two graphs and the three tables brings out the following significant facts.

TABLE II

ETHANOL OVER TITANIA

Samples taken after 0.5 g. of catalyst had been used for five minutes at 400°.

No.	Catalyst	C_2H_4, %	C_2H_6, %	CH_4, %	H_2, %	Cc. of gas per min.
22	*Ex* $Ti(OC_4H_9)_4$ (a)	75.7	15.5	4.7	4.1	..
	(b)	75.6	16.4	5.2	2.7	..
	(av.)	75.6	16.0	5.0	3.4	..
23	*Ex* $Ti(OC_2H_5)_4$ (a)	64.8	27.1	4.6	3.5	..
	(b)	62.7	28.4	5.1	3.8	..
	(av.)	63.7	27.7	4.9	3.7	30.7
24	*Ex* $Ti(OC_2H_5)_4 + B_2O_3$	66.1	27.6	2.6	3.7	33.5
25	*Ex* $Ti(OC_2H_5)_4$ + NaOH	18.9	37.3	0.0	43.8	6.0
26	Ex $Ti(OC_2H_5)_4$ + NaOH	47.6	43.2	.0	9.2	30.0

TABLE III

PERCENTAGE OF ALKENE FORMED OVER VARIOUS ZINC OXIDE CATALYSTS

Samples taken after 0.5 g. of catalyst had been in use for one hour at 400°; alcohols passed over catalyst at the rate of 50 cc. per hour.

No.	Catalyst	Ethanol, %	Propanol, %	*Iso*propanol, %	Isobutanol, %
4	Lazier's "A"	9.5	16.0	..	31.5
2	Ppt. ZnO, Weston	21.6	..	..	1.4
3	Ppt. ZnO, Lazier	9.5	6.4	..	23.0
1	Ppt. ZnO, Millington	15.7	5.7	..	1.7
8	Standard, ZnO *ex* oxalate	23.6	4.1	7.4	1.2
11	Standard + WO_3	25.2	7.4	40.6	13.3
15	Standard + H_2SO_4	21.9	3.0	8.9	1.4
9	Standard + CrO_3	30.0	4.8	9.0	1.6
16	Standard + NaOH	19.9	1.6	5.0	..
10	Standard + B_2O_3	28.1	..	7.7	..

The proportion of ethylene to hydrogen is always lower for catalysts from the precipitated zinc hydroxides than for the zinc oxide *ex* oxalate (see Fig. 2). The ratio is dependent upon the exact method of precipitation and washing and varies very widely. This variation in catalytic effect is not due to the presence of a sulfate for the same variation is found with catalysts prepared from nitrates, chlorides and acetates. There is no evidence available to show that the variation may not be due to differences in the amount of sodium hydroxide adsorbed by the precipitated zinc hydroxide.

The use of 1% of chromium, boron or tungsten oxide in a zinc oxide catalyst markedly increases the proportion of ethylene formed. The percentage of ethylene in some cases is increased by 40% of the value of the unpromoted catalyst. Vanadium and molybdenum oxides have relatively little effect in changing the ratio of dehydration and dehydrogenation of ethanol while both sulfur trioxide and sodium oxide decrease the proportion of dehydration (see Fig. 3).

The effect of a given promoter is neither qualitatively nor quantitatively constant, but is specific for a given alcohol. For instance, a sulfate lowers the percentage of alkene from ethanol and propanol and raises it for *iso*-propanol. Tungsten oxide, which shows but a slight promoter action for the formation of alkenes from ethanol and propanol, is a very active promoter for alkene formation from isopropanol and isobutanol. Chromium oxide, which is the most active of all the promoters used for ethanol, has very little effect upon the other alcohols. Boric oxide is a promoter for alkene formation from ethanol but in the concentration used is almost without effect upon isopropanol. These anomalous effects are even more marked in the case of some of the precipitated or *ex* hydroxide catalysts. For instance, Catalyst No. 3 gives only about 0.4 as much ethylene as the standard oxalate catalyst, yet it gives more propylene from propanol and almost 20 times as much isobutylene from isobutanol as does the standard oxalate catalyst. Lazier's "A" Catalyst and Millington's No. 1 Catalyst show similar divergent effects upon different alcohols.

Small amounts of sulfuric acid, sodium oxide, boron and chromium oxides in iron oxide decrease the formation of carbon dioxide from ethanol (see Table I). Of these promoters only boric oxide materially increases ethylene and ethane formation at the expense of dehydrogenation. Sodium oxide increases hydrogen at the expense of hydrocarbon, but the change is accompanied by so great a decrease in the activity of the catalyst that the change in ratio of products is of doubtful significance.

Boric oxide has little effect upon titania but sodium oxide increases ethane at the expense of ethylene, at the same time doubling the hydrogen and eliminating the formation of methane (see Table II).

It is obvious that Taylor's hypothesis and prediction as to the effect of acidic and basic promoters upon the ratio of dehydration and dehydrogenation is not supported by all of the experimental results stated above. Two promoters so unlike as sulfuric acid and sodium hydroxide show the same effect upon ethanol; that is to say, they lower the percentage of ethylene. These two promoters show opposite effects upon isopropanol (*i. e.*, they behave as predicted). It is unsafe to predict that a catalyst which shows high comparative dehydration for one alcohol will do so for another, for quite the reverse is often true. Promoters may not be classified as promoting dehydration or dehydrogenation except with reference to a specific compound.

In view of the failure of this hypothesis in the simple cases it is perhaps not necessary to raise the question as to the number and kind of ions which must be assumed to be present in a surface in order that four distinct primary reactions may occur simultaneously, as is sometimes true.

In previous papers by Bischoff, Nissen, Lazier and Adkins numerous examples have been given of the modification of the ratio of simultaneous reactions through changes in the method of preparation of the catalysts.

In the case of several of these catalysts this difference in ratio of reaction induced was really dependent upon the presence or absence of traces of certain promoters or inhibitors. In several other cases there is a *possibility* that this was true; in still other cases it seems certain that the ratio of reaction products was modified other than by the presence or absence of a promoter or inhibitor.

This was first demonstrated by Adkins for the reactions of esters over alumina from various aluminum alkoxides. It was demonstrated in the second case by Bischoff for the reactions of alcohols and other materials over titania from various sources. Lazier next obtained similar examples of selective activation with alcohols over zinc and iron oxide catalysts. The first of these attempts may be criticized in that the reactions of the esters are rather complicated and especially in that the range of selective activation was not very great. Bischoff's work may be criticized in that at that time the importance of boiling out the gases from the condensate was not realized. Moreover, it was not determined with certainty whether the C_nH_{2n+2} found was really ethane or methane or a mixture of the two. Lazier's results may be criticized in that in no case was he able to distil or otherwise rigorously purify the compound from which the catalyst was prepared.

It was of the highest importance, then, to demonstrate conclusively that the ratio of two competing reactions could be modified without the influence of a promoter. To this end tetra-ethyl and tetrabutyl orthotitanates were prepared and repeatedly distilled until they were demonstrated to be free from the usual metallic and acidic impurities. These two titanates were then hydrolyzed and used as catalysts against ethanol, using the best technique that has been developed in this Laboratory for the determination of the ratio of gaseous reaction products. The results as given in Table II are in general agreement with those of Bischoff and show conclusively that the titania from the butoxide and from the ethoxide differ very considerably in the ratio of ethylene and ethane produced while they give almost identical percentages of methane and hydrogen. These experiments demonstrate conclusively that selective activation may be obtained other than through the effect of catalyst promoters or poisons.

It is clear then (1) that the direction of shifting of the ratio of two competing reactions is not always dependent upon the acidity or basicity of the promoter, *(2)* that both the direction and amount of change in the ratio is specific for the alcohol and the catalyst and **(3)** that the ratio of competing reactions may be modified by other means than through the addition or removal of a compound from the catalyst. Some of these facts are out of harmony with the first hypothesis given in the introductory paragraph, while they are entirely in harmony with the hypothesis previously advanced from this Laboratory with regard to the possible importance of spacial relationships of the catalyst surface in determining the ratio of competing reactions. It must be admitted, however, that Adkins' hypothesis in its present form is of no value for predicting experimental results, and does not lead to positive experimental verification.

Lazier has suggested on the basis of unpublished work that the ratio of dehydration to dehydrogenation induced by a given catalyst is determined by the degree of hydration of the catalyst. Taylor called attention to this possibiiity in his address before the Colloid Symposium at Boston in 1926. The following facts would seem to have a bearing on the question. If a precipitated zinc oxide was brought up to reaction temperature (400°) and immediately used, there was first an increase in percentage of dehydration, followed by a slow decrease. This is clearly shown in Fig. 2. If, however, the catalyst was maintained at 400° in a current of dried air for fifteen minutes, there was no rise in alkene formation during the first few minutes of use (see Fig. 3). A prolonged preheating of an hour and a half increased ethylene formation by one per cent. or so over what it would have been after a fifteen-minute preheating and the rate of lowering of ethylene formation was decreased. Reheating a catalyst for thirty minutes in dry air after it has been in use for an hour or two restored the percentage of ethylene to approximately its former level. This reactivation may be repeated several times providing the catalyst has not become fouled. The passage of water vapor over the catalyst at 400" permanently impaired the dehydrating power of the catalyst, even when the catalyst was afterwards heated in dry air. These facts clearly show that the degree of hydration of the zinc oxide catalyst affects the ratio of dehydration and dehydrogenation of ethanol. It appears that the decrease in percentage of ethylene during the use of a zinc oxide is due to the accumulation of some volatile compound upon the catalyst. It seems questionable from a consideration of these facts whether the ratio of dehydration and dehydrogenation is a simple function of the degree of hydration of the catalyst.

Summary

The effect upon the ratio of simultaneous reactions of alcohols of the addition of small amounts of various acidic and basic oxides to zinc, iron, titanium and aluminum oxide catalysts has been experimentally investigated. The conclusions were reached (1) that the direction of the shift in the ratio of two competing reactions is not dependent upon the acidity or basicity of the promoter, (2) that both the direction and amount of change in the ratio is specific for the alcohol and the catalyst and (3) that the relative rate of competing reactions may be modified by means other than through the addition or removal of a compound from the

catalyst. These and other facts have been considered in their bearing upon the hypotheses which have been previously advanced to account for the variation in the ratio of competing reactions over various catalysts.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

THE SULFONATION OF PHENANTHRENE.
I. A NEW MONOSULFONATE

BY LOURS FREDERICK FIESER

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After a series of careful investigations, the results of which were published in 1902, Werner and his students[1] were able to show that three phenanthrene sulfonic acids may be obtained by the action of concentrated or fuming sulfuric acid on the hydrocarbon. Various methods of separating these isomers were elaborated and the compounds were all carefully identified and characterized. The yields, however, were poor, and the separation was a tedious process. In preparing large quantities of two of the acids according to Werner's methods, it has been found possible to introduce some improvements which render these substances more readily accessible and which also serve to cast further light on the course of the reaction.

Werner records that the best yields of the 2-acid (12%) and the 3-acid (18.6%) were obtained on heating phenanthrene with two molecular equivalents of concentrated sulfuric acid at a temperature of 120–130° for four and one-half to five hours. It was assumed that the greater part of the hydrocarbon was converted into disulfonic acids, and this conclusion has been confirmed by Sandqvist,[2] who found that disulfonic acids accompany the monosulfonic acids even when phenanthrene is sulfonated incompletely at room temperature. At a temperature of 100" or below, a third isomer, phenanthrene-9-sulfonic acid, which was not detected in the reactions carried out at 120–130°, is produced.

Before attempting to extend these observations, it seemed almost necessary to find some new method for the identification and the determination of the purity of the isomeric acids. Reactions such as the alkali fusion, or the preparation of the ester or the chloride, all require a fairly large sample of the dry salt, and they are all rather slow. A much more suitable derivative was found in the *p*-toluidine salt.. With this amine, the phenanthrene sulfonic acids all form crystalline salts whose melting points are characteristic and fairly well separated. One can quickly

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[1] Werner, Frey, J. Kunz, M. Kunz, Löwenstein, Rekner and Wack, *Ann.*, 321, 248 (1902).

[2] Sandqvist, "Studien über die Phenanthrensulfosäuren," Inaugural Dissertation, Upsala, 1912.

identify a few milligrams of an acid or of any of its metal salts, whether it is in the solid form or in solution, by this method.

In working up the reaction mixture, Werner first neutralized the acid solution with barium carbonate and thus had the tedious task of extracting the rather sparingly soluble salt of the 3-acid, and the very slightly soluble salt of the 2-acid, with water and with dilute sulfuric acid, respectively. It was found much more convenient to prepare first a sodium salt mixture and to treat a solution of this with only enough barium chloride to cause the precipitation of the barium 2-salt. When the reaction mixture was stirred mechanically and the sulfonation conducted at 120° for four hours, the yields of the 2-acid and the 3-acid were 18 and 27%, respectively. When the reaction was stopped after three hours, the amounts of the two acids corresponded to 25 and 27%, respectively, of the theoretical quantity. That the observed yield of the 3-acid did not show an increase proportional to that for the isomer is due probably to the difficulty in separating all of the 3-acid from the disulfonates. The yield of the 2-acid, on the other hand, is easily determined. That the amount of this isomer which is produced decreases with the length of the reaction period doubtless is due to the conversion of the acid into disulfonic acids, as will be shown in the following paper.

The modified method of separation was also applied to the mixtures which result from the low-temperature sulfonation, and which are known to contain the 2-acid, the 3-acid and the 9-acid. Thus Werner[3] obtained these acids in 7, 9 and 6% yield, respectively, by sulfonating at 100° for eight hours, while Sandqvist raised the yield of the 9-acid to 7–14.5% by carrying out the reaction at 20° over a period of fifteen to twenty days.[2,4] In the present work the sulfonation was conducted at 60° for three days and the mixture was stirred mechanically for about half of the time. The 2-acid was easily removed in the form of the barium salt, and a considerable quantity of the 3-acid separated as the least soluble fraction on crystallizing the remaining product in the form of the potassium salt. The further working of the mixture involved many difficulties, most of which have been recognized by the earlier investigators. The mixture, however, is even more complex than these workers have realized, for it contains not only the 3-acid and the 9-acid, but traces of the 2-acid and an appreciable amount of a new isomer, phenanthrene-1-sulfonic acid. The presence of the 1-acid was only established in the present work through a fortunate circumstance. A sulfonate residue, which had yielded no pure products after several crystallizations, was fused with alkali in the hope that the phenanthrol mixture, particularly if it contained

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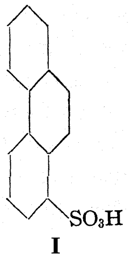
[3] Werner, ref. 1; see also J. Kunz, "Ueber einige Derivate des Phenanthrens," Inaugural Dissertation, Zürich, 1902, p. 35.

[4] Sandqvist, Ann., 392, 76 (1912).

any dihydroxyphenanthrenes, might be separable. While this was not the case, it was found that the acetate mixture obtained on acetylation easily yielded pure 1-acetoxyphenanthrene on crystallization. It was then found possible to isolate the 1-acid from a similar sulfonate mixture, but the process is extremely tedious. The solubilities of the salts of the 1-acid, the 3-acid and the 9-acid all appear to be about the same, and the solutions have a pronounced tendency to remain supersaturated.[5] By carrying out a great many crystallizations of the potassium and ferrous salts, and by identifying the various fractions by means of the melting points of the p-toluidine salts, a part, at least, of the sulfonate mixture was separated into the pure components, the yields being as follows: 2-acid, 18%; 3-acid, 18%; 9-acid, 13%; 1-acid, 8%.

The sulfonation of phenanthrene at a low temperature thus gives a mixture of four of the five possible monosulfonic acids. Two of these acids, the 9-acid and the 1-acid, have not been found in mixtures obtained at 120–130°. Experiments with the former acid, as well as with the 2-acid and the 3-acid, failed to reveal any rearrangement on heating with sulfuric acid but indicated that the substances are all sulfonated further with great ease. Thus it is probable that the absence of two of the acids from the products obtained at the higher temperature is due simply to the disulfonation of these substances. The sulfonation of phenanthrene leads to the same number of isomers as the nitration, but neither the relative yields nor the positions of the substituents are the same; nitration, according to Schmidt and Heinle,[6] yields 9-nitrophenanthrene as the chief product, together with smaller quantities of the 2-nitro and 4-nitro and a very small amount of the 3-nitro derivatives.

Phenanthrene-1-sulfonic acid, I, was characterized by the preparation of the potassium and p-toluidine salts, the methyl ester and the corresponding quinone, II. The structure was established by conversion into 1-phenanthrol, III, which, unknown at the time of these experiments, has been synthesized recently by Shoesmith and Guthrie.[7] The properties agreed with the description given by these authors, while the methyl ether



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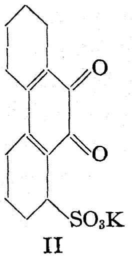

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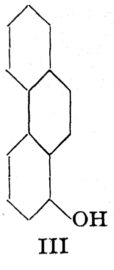
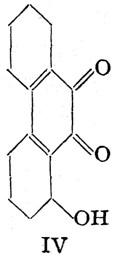


III



IV

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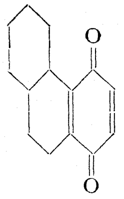
[5] Compare Sandqvist, ref. 2, p. 36.

[6] Schmidt and Heinlt, *Ber.*, 44, 1488 (1911).

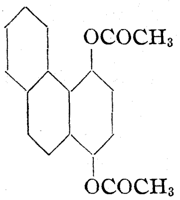
[7] Shoesmith and Guthrie, J. Chem. *Soc.*, 2332 (1928).

and its picrate melted at the temperatures given by Pschorr, Wolfes and Buckow[8] for the synthetically prepared 1-methoxyphenanthrene and its picrate. From the acetate, which was oxidized and hydrolyzed, there was obtained I-hydroxyphenanthrenequinone, IV, which is the last of the four possible compounds of this type to be described.

Another compound obtainable from 1-phenanthrol, and one which is of particular interest in connection with the problem outlined in the first paper of this series,[9] is 1,4-phenanthrenequinone, V. This was prepared in good yield by- coupling I-phenanthrol with diazotized sulfanilic acid, reducing the azo dye and oxidizing the 4-amino-1-phenanthrol. On reductive acetylation to VI, followed by oxidation, the diacetyl derivative of 1,4-dihydroxy-9,10-phenanthrenequinone (VII) was obtained. This compound has been described by Brass and Stadler,[10] who adequately established the positions of the substituent groups, and the author is greatly indebted to Professor Brass for supplying him with a sample of the product. The substance was found to be identical with the material here described. The structure of the new isophenanthrenequinone, V, is thus definitely fixed, and it is also clear that both 1-phenanthrol and 3-phenanthrol[9] couple in the 4-position and behave, in this respect, like naphthols. With the isolation of V, all of the four possible homonuclear phenanthrenequinones are known.



V



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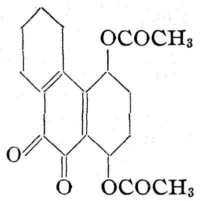

VII

Experimental Part

***p*-Toluidine** Salts of the Phenanthrene **Sulfonic** Acids.—In order to prepare such a salt the aqueous solution of the free acid, or of the sodium, potassium or ferrous salt, is treated with an excess of *p*-toluidine and hydrochloric acid, enough water is added to bring all of the material into solution at the boiling point and crystallization is allowed to take place. A barium salt should be boiled with dilute sulfuric acid, a little animal charcoal added and the filtered solution treated with *p*-toluidine. If the amine salt separates in an oily condition, the walls of the containing vessel should be thoroughly scratched, for these salts, particularly that of the 3-acid, may remain as oils for a short time even when nearly pure.

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[8] Pschorr, Wolfes and Buckow, Ber., **33,** 170 (1900).

[9] Fieser, THIS JOURNAL, 51, 940 (1929).

[10] Brass and Stadler, ***Ber.,*** 57, 134 (1924).

On the other hand, a fairly impure acid, or a mixture of pure isomers, gives a *p*-toluidine salt which remains as an oil almost indefinitely. This property characterizes a mixture of isomers nearly as definitely as the depression in the melting point, though this is large. In determining the melting point of one of the salts, the sample may be dried by pressing the material on a filter paper, but the capillary should not be placed in the melting-point bath when the temperature is greater than 130°, for, if the heating is commenced at a higher temperature, the material melts 20–30° below the true melting point. When the material is thoroughly dried in a vacuum at 100°, this behavior is not noted. The salts all sinter at temperatures slightly below the melting points. They are all moderately soluble in hot water, sparingly soluble in cold water and very readily soluble in alcohol.

TABLE I

p-TOLUIDINE SALTS, $C_{21}H_{19}O_3NS$

Salt of phenanthrene-( )-sulfonic acid	Melting point, °C.	Appearance	Analyses, % C (calcd., 69.01)	Analyses, % H (calcd., 5.24)
-1-	260 (267 corr.)	Needles	68.75	5.47
-2-	282 (291 corr.)	Flat needles or plates	68.82	5.17
-3-	217 (222 corr.)	Thick needles	68.85	5.47
-9-	229 (235 corr.)	Small needles	68.68	5.47

Sulfonation at 120–125° for Four Hours.—Three hundred and twenty-seven cc. of concentrated sulfuric acid was added to 500 g. of pure phenanthrene[11] in a 2-liter flask and the mixture was heated in an oil-bath and stirred by hand until it became sufficiently liquid to permit mechanical stirring. The temperature of the reaction mixture soon reached 120° and a temperature of 120–125° was maintained for just four hours. The reaction is exothermic, even after the disappearance of all of the phenanthrene, and the bath must be kept at a temperature about 4° below that of the mixture. The product first became green and some sulfur dioxide was formed; a dark brown sirup finally resulted. After heating and stirring for the time specified, this solution, while still hot, was dissolved in 3.5–4 liters of water and a concentrated solution of 400 g. of sodium hydroxide was added. After thorough cooling in an ice-bath, the precipitated sodium salt was collected on a large funnel, pressed well and washed well with a half-saturated sodium chloride solution. The filtrate contains a mixture of disulfonates.

The crude mixture of sodium salts was dissolved in 6–7 liters of water, to which there was added enough hydrochloric acid to render the solution slightly acid,[12] and a solution of 100 g. of barium chloride dihydrate was added to the boiling solution. After digestion of the fine precipitate of barium phenanthrene-2-sulfonate for a short time, the mixture was brought onto the funnel while at the boiling point. The filtrate, from which some material crystallized at once, was set aside to cool. The precipitated barium salt was digested at the boiling point with 6–7 liters of water and again collected. The filtered wash water contained, as shown by the melting point of a sample of the *p*-toluidine salt, only barium phenanthrene-3-sulfonate, which crystallized out after concentration of the solution. The main barium salt precipitate still contained a small amount of the 3-

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[11] From the Gesellschaft für Teerverwertung, Duisberg-Meiderich.

[12] The solubility of the sulfonates is increased by the presence of a mineral acid but phenanthrene itself dissolves in a too strongly acidic solution.

salt, but the latter was removed, along with a little of the 2-salt, by a further boiling with 6–7 liters of water. This left the barium salt of the 2-acid in an essentially pure condition. The salts remaining in the last wash water were recovered by concentrating the solution, and they were separated by converting the barium salt mixture into a mixture of the potassium salts, dissolving this in boiling water, and adding 2 g. of barium chloride dihydrate. The precipitated salt, after washing with hot water, was the pure barium 2-sulfonate (2 g.), while the mother liquor yielded 9 g. of the 3-sulfonate.

The first filtrate from the precipitation of the main portion of the barium 2-sulfonate deposited crystals of the pure barium 3-sulfonate on cooling. The mother liquor was concentrated to a fairly small volume and saturated sodium chloride solution was added. The precipitated sodium salt was found to consist chiefly of the 3-sulfonate, and it was easily purified, after conversion into the potassium salt, by crystallization (76 g.). The mother liquor remaining from the salting-out with sodium chloride contained an appreciable amount of the 3-sulfonate, mixed probably with disulfonates, but its recovery is not easily accomplished. On boiling down the solution to a volume of 1 liter, a crystalline paste was obtained, and this was converted into the potassium salt and crystallized several times. It finally yielded 31 g. of the pure 3-sulfonate.

The total yield of barium phenanthrene-2-sulfonate was 175 g., while 146 g. of the barium salt and 107 g. of the potassium salt of phenantbrene-3-sulfonic acid were obtained. Determinations of the melting points of the *p*-toluidine salts showed that the products were free from all but traces of isomers, and the salts of the 3-acid, having been crystallized, were free from much inorganic material. The barium salt of the 2-acid contained only a small amount of barium sulfate, and from the results of alkali fusions it was judged that the material was 95% pure. On this basis the yields were: 2-acid, 18%; 3-acid, 27%.

Sulfonation at 120–125° for Shorter Periods of Tie.—When the sulfonation was carried out in the manner described above, with the exception that the reaction was stopped after two and one-half hours, a small amount of phenanthrene was unsulfonated. Only traces of phenanthrene remained when the reaction proceeded for three hours, and the yields were practically the same as for the shorter period. It is thus considered that ***the conditions most suitable for the preparation of the 2-acid and the 3-acid are: sulfonation for three hours with two molecular equivalents of concentrated acid at 120–125°.***

Owing to the increase in the yields when operating under the conditions specified, the washing of the precipitate of barium phenanthrene-2-sulfonate is not easily accomplished when working on a large scale and a slight modification of the above procedure is advisable. Instead of precipitating the barium salt from a solution of the crude sodium salt, the sodium salt was dissolved in water containing 50 cc. of concentrated hydrochloric acid (to aid in the dissolution of the salt) and the filtered solution was then neutralized with sodium hydroxide and allowed to crystallize. The crystals, consisting largely of the salt of the 2-acid, were dissolved in about 8 liters of water, 100 g. of barium chloride dihydrate was added, and the precipitate was collected and then digested with 6 7 liter portions of boiling water until the residual salt was found to be free from the isomers. It was often found that a single washing was sufficient for this purpose. The washings were concentrated to a small volume, sulfuric acid was added to precipitate the barium and the filtered solution was treated with potassium hydroxide to bring down a potassium salt mixture, which was set aside. The mother liquor from the sodium salt crystallization was concentrated and the product converted into the potassium salt. This was combined with the other batch of potassium salt and crystallized from water, giving a large quantity of the pure potassium 3-salt. The mother liquor, containing more of this salt together with some of the 2-salt, was concentrated, and the product was salted out with potassium chloride and washed free of sulfate ion.

A solution of this material was then treated with 10 g. of barium chloride dihydrate, the precipitate of the barium 2-salt was washed free of isomers and the washings were discarded. From the mother liquor there was obtained an additional quantity of the potassium 3-salt. The yields were: barium phenanthrene-2-sulfonate, 232 g. (25%); potassium phenanthrene-3-sulfonate, 225 g. (27%).

The Preparation of the **Phenanthrols.**—Werner[1] prepared 2-phenanthrol from the potassium salt of the 2-acid. If it is desired to prepare this salt from the barium salt, it is highly advisable to use the salt in the moist and finely divided condition in which it is first obtained; but the reaction with sulfuric acid is slow at best, and one should employ several fresh portions of acid. Barium sulfate carried through the filter is easily removed with animal charcoal. It is not necessary, however, to follow this rather tedious procedure, for the barium salt, prepared as described above, may be fused without difficulty. Thus 150 g. of the finely powdered salt was stirred into a melt from 450 g. of potassium hydroxide at a temperature of 290–300° in the course of fifteen minutes; the temperature was then raised to 325° and held there for five minutes. The fusion was then complete and a brown, oily layer of the phenanthrolate appeared at the top of the melt. After some cooling, but before solidification, the mass was added in small portions to a mixture of 1 liter of concentrated hydrochloric acid and about 2 kg. of ice. After thorough stirring, the phenanthrol, which was mixed with some barium sulfate, was collected, dissolved in dilute alkali and repreeipitated. The material at first separates in a finely divided condition, but when it is digested at the boiling point the particles soon become more compact and the material may be collected and washed very easily. The crude product is most conveniently purified by distillation at a pressure of 3 mm. If the barium salt used is free from any isomers, the 2-phenanthrol so prepared is completely pure and melts at 168°. The average yield was 65 g. (72%), about 8–10% of the precipitated material having been lost in the distillation. Pure 2-phenanthrol may be obtained from a mixture containing the more soluble 3-phenanthrol by crystallization from benzene, but only with the loss of a considerable amount of material. 3-Phenanthrol may be prepared in a similar manner, or from the potassium salt, and purified as suggested by Smith,[13] by-distillation in *vacuo.*

Sulfonation at **60°.**—Four hundred grams of finely powdered phenanthrene was mixed with 160 cc. of concentrated sulfuric acid and the temperature was kept at 60°. The mixture, which was frequently stirred, soon became pasty and somewhat green, and some sulfur dioxide was formed. After twenty-four hours, 80 cc. of concentrated acid was added and the mixture was stirred mechanically throughout that, and the following, day. After the reaction had proceeded for a total of three days, a viscous, bluish-green, homogeneous sirup resulted; this was dissolved in water and the solution was treated with an excess of sodium hydroxide (400 g.). The product contained some phenanthrene, which was removed by boiling a solution of the salt with animal charcoal. The filtered solution was allowed to cool and the crystalline product was subjected to the usual process of separating out the pure barium salt of phenanthrene-2-sulfonic acid, using 40 g. of barium chloride dihydrate. All mother liquors and washings were then concentrated and the material converted into the potassium salt, which was precipitated several times with potassium chloride solution in order to remove all sulfates and disulfonates. After three crystallizations of this potassium salt, a considerable quantity (95 g.) of the pure potassium 3-salt was obtained. The mother liquors were then combined and the product was converted into a ferrous salt mixture by the action of ferrous sulfate and dilute sulfuric acid. On crystallizing this salt several times, excellent needles of the ferrous salt of the 9-acid finally resulted, and from this material 70 g. of pure potassium phenanthrene-9-sulfonate was obtained by the action of po-

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[13] Smith, J. *Chem. Soc.*, 109, 569 (1916).

tassium hydroxide. The material in the mother liquors was then converted into the potassium salt and this, after being freed from sulfates, was dissolved in water and treated with 5 g. of barium chloride dihydrate in order to precipitate a small quantity of the 2-acid still present.[14]

From this point on the separation of the combined product, which was collected in the form of the purified potassium salt, is extremely difficult and no systematic method of procedure can be specified. The mixture contains the 3-acid, the 9-acid and the 1-acid and, as stated in the introduction, the solubilities of the salts of these acids are all very nearly the same, and the separation is greatly complicated by the tendency to form supersaturated solutions. A systematic fractionation was undertaken at the outset, and potassium phenanthrene-1-sulfonate was first isolated from an intermediate fraction. The concentration of a preponderant quantity of this salt in a given fraction becomes apparent from the character of the p-toluidine salt which is obtained from it. The amine salt of this impure acid usually separates in the form of oily shreds which fail to solidify or else the solution sets to a gel. On further crystallization of the potassium salt a purification can be effected until excellent, large plates of the 1-salt are obtained, and the p-toluidine salt now has little tendency to remain in an oily or colloidal condition, but forms small, fine needles.

Little regularity was observed in the order in which the three potassium salts crystallize from the mixtures; the 3-salt may separate first, followed by the 1-salt, and then by more of the 3-salt. After dividing the material into six fractions, all solutions appeared to contain all three acids, with the exception of the "least soluble" fraction, which contained none of the 9-acid. It appears that the potassium 9-salt has somewhat less tendency to crystallize from the mixture than the other two, while the ferrous salt of the 9-acid tends to separate first. As a consequence, it is advisable to change occasionally to the ferrous salt and thus remove some of the 9-acid. The 1-acid and the 3-acid were isolated in pure condition only in portions of 0.5–2 g. at a time. This was done by carrying out numerous crystallizations, by carefully noting the appearance of the crystals separating, interrupting the process whenever a change or a pause in the crystallization was observed, and by identifying the products by means of their p-toluidine salts.

The separation finally effected was far from being complete; it was interrupted with 110 g. of the potassium salt mixture still on hand. The amounts of the salts isolated in pure condition were as follows: barium phenanthrene-2-sulfonate, 131 g. (18%); potassium phenanthrene-3-sulfonate, 127 g. (19%); potassium phenanthrene-9-sulfonate 86 g. (13%); potassium phenanthrene-1-sulfonate, 27 g. (4%).

The residual sulfonate mixture was partially identified as follows. It was subjected to alkali fusion and the phenanthrol mixture was distilled and then acetylated. After crystallizing this acetate mixture twice from alcohol, 20 g. of pure 1-acetoxyphenanthrene, m. p. 135–136°, was obtained, which brings the amount of phenanthrene-1-sulfonic acid which is known to have been produced in the sulfonation up to 8%.

Phenanthrene-1-sulfonic Acid

Metal Salts.—The potassium salt crystallizes from water in the form of large plates. The solubility in water is about the same as that of the 3-isomer. The salt is only sparingly soluble in alcohol, but dissolves readily in glacial acetic acid.

Anal. Calcd. for $C_{14}H_9O_3SK$: K, 13.19. Found: K, 13.22.

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[14] It may be noted that the salts of the 2-acid remain in solution up to this point even though they are much less soluble than the salts of the isomers. According to Sandqvist (ref. 2, p. 8), the ferrous 2-sulfonate is but one-fourth as soluble at 20° as the ferrous 9-sulfonate,

The barium salt dissolves with difficulty in boiling water, but it only crystallizes from the well-concentrated solution. The ferrous salt crystallizes in the form of needles; it appears to be slightly more soluble than ferrous phenanthrene-9-sulfonate.

Methyl Ester.—A suspension of the potassium salt in dimethyl sulfate was boiled gently until all of the salt dissolved, and then heated on the water-bath for one hour. The solution was poured into water, the mixture was boiled for a few minutes in order to decompose the dimethyl sulfate and well cooled. The product was purified by crystallization from methyl alcohol, in which it dissolves readily; it formed colorless plates melting at 102°.

Anal. Calcd. for $C_{15}H_{12}O_3S$: C, 66.15; H, 4.45. Found: C, 65.87; H, 4.47.

Potassium **Phenanthrenequinone-1-sulfonic** Acid.—Three grams of potassium phenanthrene-l-sulfonate was dissolved in 25 cc. of glacial acetic acid and a solution of 3 g. of chromic acid in water, diluted with glacial acetic arid, was added while the temperature was kept at 100° by cooling. The yellow quinone, which began to separate after a few minutes, was brought into solution and allowed to crystallize slowly. The product (1.7 g.) was washed with alcohol and purified by adding about one volume of alcohol to four volumes of an aqueous solution and allowing crystallization to take place very slowly. Under these conditions large, orange-yellow plates were formed.

Anal. Calcd. for $C_{14}H_7O_5SK$: K, 11.98. Found: K, 11.94.

The quinone is very readily soluble in water and the yellow aqueous solution rapidly loses its color on the addition of alkali. The solution in concentrated sulfuric acid is deep red.

Derivatives of 1-Phenanthrol

Most of the material used for the following reactions was prepared from the acetate, which, in turn, was obtained from the mixture of the phenanthrene monosulfonates. The acetate appears to be much less soluble in alcohol than any of the isomers present and the isolation of the pure material is accomplished with ease. A fairly large quantity (6–10 g. from 100 g. of phenanthrene) may be obtained from the sulfonate mixture which remains after separating the greater part of the 2-acid, the 3-acid and the 9-acid.

1-Acetoxyphenanthrene crystallizes from alcohol or benzene in the form of long needles melting at 135–136°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.00; H, 5.14.

1-Phenanthrol.—Twenty grams of the acetate was warmed with 80 cc. of alcohol and 15 cc. of 6 N sodium hydroxide until the material dissolved. The solution was diluted with an equal volume of water and acidified, when the phenanthrol separated in the form of small, colorless needles; yield, 16 g. (97%), m. p., 155°. Fusion of pure potassium phenanthrene-l-sulfonate (10 *g.)* with potassium hydroxide (35 g.) at 300' gave a product which, after crystallization from benzene–ligroin, formed cotton-like clusters of colorless needles melting at 155° (157° corr.) and identical with the above product.

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.57; H, 5.19, Found: C, 86.34, H, 5.27

The properties are in conformity with the observations of Shoesmith and Guthrie,[7] who prepared 1-phenanthrol synthetically.

1-Methoxyphenanthrene was prepared by the action of dimethyl sulfate and alkali. It formed long needles melting at 105° and the picrate melted at 154° corr. Pschorr, Wolfes and Buckow[8] give 105–106° and 153" corr., as the melting points of these substances.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.50; H, 5.81. Found: C, 86.35; H, 5.68.

1-Acetoxyphenanthrenequinone.—A solution of 1 g. of 1-acetoxyphenanthrene in

6 cc. of glacial acetic acid was treated with a solution of 1.2 g. of chromic acid at 70° and the temperature was kept at this point until the solution required no further cooling. The quinone, which separated on cooling, was washed with alcohol and with water, when it was nearly pure; m. p. 201°; 0.6 g. It dissolved readily in glacial acetic acid and the solution deposited orange, cluster-forming needles melting at 202° (206° corr.).

Anal, Calcd. for $C_{16}H_{10}O_4$: C, 72.17; H, 3.79. Found: C, 71.80; H, 4.08.

1-Hydroxyphenanthrenequinone.—The above acetate forms a soluble bisulfite addition product which, in a hot solution, readily undergoes hydrolysis with the formation of hydroxyphenanthrenequinone. The latter substance, being insoluble in sodium bisulfite solution, thus separates in crystalline condition. The red product which was obtained in this way was crystallized from alcohol. It dissolves readily in this solvent and the orange solution deposits very long, fiery red needles melting at 220° (227° corr.).

Anal. Calcd. for $C_{14}H_8O_3$: C, 74.98; H, 3.60. Found: C, 74.64; H. 3.89.

The solution of the quinone in concentrated sulfuric acid has an intense green color. The material dissolves in very dilute sodium hydroxide solution with the development of a grape-purple color, and the slightest excess of alkali precipitates an indigo-blue sodium salt.

The Preparation of 1,4-Phenanthrenequinone

The conversion of 1-phenanthrol into this quinone, through the azo dye and 4-amino-1-phenanthrol, was accomplished in the manner found useful for the isomeric ortho quinones,[9,15] though the yield was poorer, and the aminophenanthrol is more sensitive, than in the other cases. In the preparation of the quinone it is advisable to carry out the complete series of reactions without isolating any of the intermediates.

A solution of 2.1 g. of crystalline sulfanilic acid in 16 cc. of 0.6 N sodium hydroxide was diazotized by adding 0.7 g. of sodium nitrite and pouring the solution into a mixture of 2.5 cc. of concentrated hydrochloric acid and ice. This was coupled with a solution of 1.94 g. of 1-phenanthrol in 30 cc. of water and 5 cc. of 6 *N* sodium hydroxide. To the deep red solution of the azo dye which resulted, sodium hyposulfite solution was added and the mixture was heated until the 4-amino-1-phenanthrol which separated was completely colorless. The product was collected in an atmosphere of nitrogen, for it is ertremely sensitive to air-oxidation, it was quickly made into a very fine paste with about 100 cc. of water containing sulfur dioxide and 2.0 cc. of concentrated hydrochloric acid was added. The mixture was stirred very vigorously and heated to a temperature just below the boiling point. The pink solution was filtered from a small amount of undissolved material and this was warmed with a fresh quantity of dilute acid. The combined filtrates were cooled to room temperature, when a part of the amine hydrochloride was deposited as a fine powder. A solution of 1.2 g. of chromic acid and 1.2 cc. of concentrated sulfuric acid was then added, causing the separation of the yellow quinone in a finely divided condition. The mixture was warmed to 45° to increase the particle size and to complete the oxidation, before collecting the product. The crude material (1.2 g.) melted at 147" and contained a small amount of a black, insoluble substance. It is best purified by crystallization from ligroin with the use of animal charcoal. Pure 1,4-phenanthrenequinone forms light, fluffy, yellow needles melting at 153° (155" corr.); yield, 0.8 g. It dissolves readily in alcohol, benzene or glacial acetic acid; the solution in concentrated sulfuric acid is violet-red in color. The quinone dissolves only very slowly in acetic anhydride containing sulfuric acid.

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.76; H, 3.88. Pound: C, 80.42; H, 3.88.

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[15] Fieser, THIS JOURNAL, 51, 1896 (1929).

The hydrochloride of 4-amino-1-phenanthrol may be precipitated by adding hydrochloric acid to a solution of the salt, but it separates in the form of a gray powder and does not crystallize well. It was characterized by the preparation of a triacetyl derivative.

Triacetyl-4-amino-1-phenanthrol.—The hydrochloride (0.5 *g.)* was heated for one hour on the water-bath with an excess of acetic anhydride (5 ec.), 0.3 g. of fused sodium acetate was then added to complete the reaction and, after five minutes, the solution was poured into water. The product solidified rapidly and, when triturated with a little ether to remove some brown material, it was nearly pure. The substance dissolves very readily in methyl alcohol and the solutions have a decided tendency to remain in a supersaturated condition. When the solution is cooled rapidly and seeded, small colorless plates melting at 143° are obtained.

Anal. Calcd. for $C_{20}H_{17}O_4N$: C, 71.63; H, 5.11. Found: C, 71.56; H, 5.33.

1,4-Diacetoxyphenanthrene.—This compound was obtained by heating equal parts of 1,4-phenanthrenequinone, zinc dust and sodium acetate with 5 parts of acetic anhydride until the solution became practically colorless. The solution was diluted with glacial acetic acid, filtered, and poured into water, when the diacetate soon separated in nearly pure condition; yield, 95%; m. p. 137–138". It crystallizes well from ligroin, forming slender long needles melting at 140°.

Anal. Calcd. for $C_{18}H_{14}O_4$: *C,* 73.45; H, 4.79. Found: C, 73.17; H, 4.89.

1,4-Diacetoxy-9,10-phenanthrenequinone.—The oxidation of the diacetoxyphenanthrene does not proceed smoothly and care must be taken to avoid the hydrolysis of the product during crystallization. The oxidation was carried out in glacial acetic acid solution at 40°, using 1 g. of chromic acid to 1 g. of the diacetate. On completion of the reaction, the solution was diluted with water. An orange, semi-solid oil separated and this was triturated with cold alcohol in order to dissolve the oil and leave a clean yellow solid (0.3 g.). After two crystallizations from benzene–ligroin, golden yellow prisms melting at 181° (184° corr.) were obtained.

Anal. Calcd. for $C_{18}H_{12}O_6$: C, 66.65; H, 3.73. Found: C, 66.54; H, 3.81.

This compound has been described by Brass and Stadler,[10] who report a melting point of 183°. Through the kindness of Professor Brass in supplying a sample of 1,4-dihydroxyphenanthrenequinone, a direct comparison of the two products was possible. The sample was acetylated and the product crystallized from benzene–ligroin, when it melted at 181° and gave no depression on admixture with the above quinone. Color tests confirmed this identification.

Summary

Some improvements have been effected in the method of separating and identifying phenanthrene-2-sulfonic acid and phenanthrene-3-sulfonic acid, the chief products resulting from the sulfonation of the hydrocarbon at 120–130°. It was known that phenanthrene-9-sulfonic acid is also produced when the reaction is carried out at a lower temperature. In the course of the present work, a fourth isomer was discovered among the products of the low-temperature sulfonation and the new substance was found to be phenanthrene-1-sulfonic acid. It has been used in the preparation of a few new phenanthrene derivatives, the most interesting of which are 1-hydroxy-9,10-phenanthrenequinone and 1,4-phenanthrenequinone.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

THE SULFONATION OF PHENANTHRENE.
II. DISULFONATION

BY LOUIS FREDERICK FIESER

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It was observed as early as 1873 that disulfonic acids are produced in the sulfonation of phenanthrene along with the monosulfonic acids, even when the reaction is stopped before all of the hydrocarbon has been consumed,[1] and yet there is no information available concerning the nature of these disulfonic acids. When the sulfonation is conducted at 120–130°, under the conditions best suited for the preparation of the 2- and the 3-monosulfonates, over 40% of the phenanthrene is converted into disulfonates.[2] Having collected a certain quantity of this material as a by-product, it became a matter of interest to attempt to learn something of the composition of the mixture.

A method of isolating a mixture of the potassium disulfonates in a form free from inorganic salts was found, and some attempts were made to effect a separation of the isomers. This difficult task, however, was not accomplished. Among the obstacles, the extreme solubility of the potassium salts may be mentioned. Potassium sulfate crystallizes out first from a solution of the organic and inorganic salts; even the barium salt is very soluble. The tendency to form supersaturated solutions, so often noted with phenanthrene derivatives, is particularly marked with these salts. In addition to these unfavorable properties, one is confronted with an extremely complex mixture. From the results to be presented below, it may be said that there are probably twelve isomers present in the mixture.

In order to simplify the problem, a study was made of the disulfonic acids produced when pure phenanthrene-2-sulfonic acid and the 3-isomer are treated with sulfuric acid at 120–130°. In each case there was obtained a mixture of extremely soluble disulfonates having the unfavorable properties noted above, and a separation was not achieved. The mixtures were fused with alkali, but the phenanthrol mixtures, though easily purified by distillation at a reduced pressure, likewise resisted efforts to effect a separation. When the phenanthrol mixtures were acetylated, on the other hand, it was possible, by fractional crystallization, to isolate three pure diacetoxyphenanthrenes as the result of each sulfonation. While it is a relatively easy matter to separate the greater part of the chief constituent of each mixture, the isolation of the substances formed in smaller quantity was accomplished only after a great many fractionations.

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[1] Graebe, Ann., 167, 152 (1873). See the preceding paper for further references.

[2] Fieser, THIS JOURNAL, 51, 2460 (1929).

As in the separation of the phenanthrene-monosulfonic acids, one encounters here the phenomena of supersaturation and of an order of Crystallization which is contrary to the solubility relationships. Though the separations were thus incomplete, it will be seen from the following results that a fairly comprehensive account is given of the course of the sulfonations. From potassium phenanthrene-3-sulfonate, there was obtained, on sulfonation and fusion, a phenanthrol mixture corresponding to 83% of the theoretical amount, while the distilled material amounted to 77%. Conversion into the diacetate was quantitative and 70% of this was separated into the pure constituents. The melting points of the isomers, and the amounts which were obtained in pure condition from the mixtures, are given in the following table.

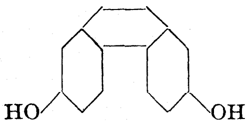
TABLE I

DIACETOXY-PHENANTHRENES OBTAINED

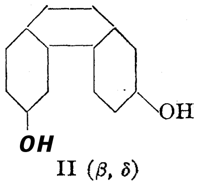
	From phenanthrene-3-sulfonic acid			From phenanthrene-2-sulfonic acid		
	α	β	γ	6	ε	ζ
M. p., °C.	124.5	122–123	184	122–123	181.5	125
Yield, %	59.1	10.0	0.9	54.1	2.1	1.0

The problem of determining the positions of the substituents in these compounds is to some extent simplified by the fact that they all yield diacetoxy-9,10-phenanthrenequinones on oxidation, showing that the second substituent has in no case entered the 9- or 10-position. While none of the phenanthrene derivatives correspond to known compounds, the quinone obtained from one of them, namely, ε-diacetoxyphenanthrenequinone, was found to be identical with 2,7-diacetoxyphenanthrenequinone which has been described by several investigators.[3,4] This proves that the ε-isomer, melting at 181.5°, is the diacetate of 2,7-dihydroxyphenanthrene, I.

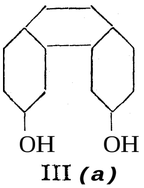
A further fact of value in the elucidation of the structural problem is that two of the substances listed in Table I are identical.



I (ε)



II (β, δ)



III (α)

The β-diacetate, which constitutes 10% of the product obtained from the 3-sulfonic acid, is identical with the δ-diacetate, which is the chief product

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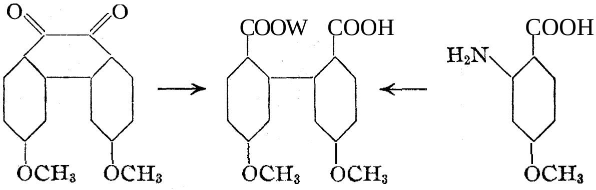
[3] (a) Anschütz and Meyer, *Ber.*, 18, 1944 (1885); (b) Schmidt and Kämpf, *ibid.*, *36,* 3742 (1903); (c) Werner, *ibid.*, 37, 3087 (1904); (d) Brass and Nickel, *ibid.*, 58, 208 (1925).

[4] Through the courtesy of Professor Brass, to whom the author wishes to express his thanks, a direct comparison of the two substances was possible.

resulting from the sulfonation of the 2-sulfonic acid. Assuming that no rearrangement has taken place, the diacetate which is obtained from both the 2-acid and the 3-acid must have a structure corresponding to 2,3-dihydroxyphenanthrene, or to 2,6(or 3,7)-dihydroxyphenanthrene, II. The former structure is not only improbable, but is definitely ruled out because the dimethyl ether and the dihydroxyphenanthrenequinone derived from the new dihydroxyphenanthrene are different from the known 2,3-dimethoxyphenanthrene[5] and 2,3-dihydroxyphenanthrenequinone.[6] The substance, therefore, may be assigned the structure of II.

From the foregoing it is seen that in three instances, in the production of a disulfonic acid from a monosulfonic acid, the second substituent has entered the unsubstituted, terminal benzene ring. It is not unreasonable to suppose that this rule also holds for the formation of the acid of the a-series, whence the substituents in this series are probably-in the 3,5-, the 3,6- or the 3'8-positions, since the 3,7-isomer is already known. It will be observed that the isomer in question is the chief reaction product. Recalling the fact that the monosulfonation of phenanthrene gives the 3- and the 2-acids as the chief products, while a relatively small amount of the 1(or 8)-acid, and none of the 4(or 5)-acid, is formed, it will be seen that the most probable structure for the a-series is represented by III, the 3,6-derivative.

The correctness of this conclusion was proved in the following manner. The dimethyl ether of the a-series was oxidized to a quinone, IV, and this was oxidized by hydrogen peroxide in glacial acetic acid solution. Two products were obtained, one having the properties of a lactone, the other (V) giving reactions characteristic of a diphenic acid, such as the formation of a fluorenorie on treatment with sulfuric acid. The same diphenic acid, V, was obtained synthetically from 4-methoxy-2-aminobenzoic acid, VI.



IV V VI

The formation of the lactone in the oxidation of 3,6-dimethoxyphenanthrenequinone represents a somewhat unusual reaction. The substance has the formula $C_{15}H_{12}O_4$. It dissolves in alkali only on long boiling. That this is not due to a lack of solubility of the sodium salt but to the slow opening of a lactone ring is shown by the result of methylation in

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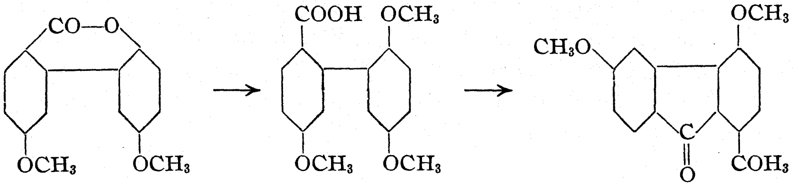
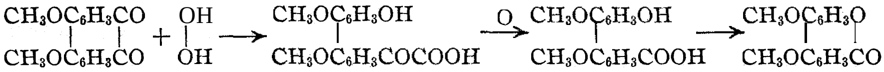
[5] Pschorr and Buckow, *Ber.*, **33, 1831** (1900).

[6] Brass, Ferber and Stadler, *ibid.*, 57, 127 (1924).

alkaline solution (followed by boiling with alkali), for a substance differing from the lactone by the elements of methyl alcohol is thus obtained and the new compound dissolves in cold carbonate solution. This methylated derivative yields a trimethoxyfluorenone on dissolution in concentrated sulfuric acid, indicating the presence of a carboxyl group adjacent to a diphenyl linkage. These facts point to the structures VII, VIII and IX for the compounds concerned. The lactone, VII, could not be obtained on treating 5,5′-dimethoxydiphenic acid with hydrogen peroxide, and it must, therefore, come directly from 3,6-dimethoxyphenanthrenequinone. It is probably produced as follows



VII VIII IX



$$\begin{array}{l}CH_3OC_6H_3CO\\ \quad | \qquad\quad |\\ CH_3OC_6H_3CO\end{array} + \begin{array}{l}OH\\ |\\ OH\end{array} \longrightarrow \begin{array}{l}CH_3OC_6H_3OH\\ \quad |\\ CH_3OC_6H_3COCOOH\end{array} \xrightarrow{O} \begin{array}{l}CH_3OC_6H_3OH\\ \quad |\\ CH_3OC_6H_3COOH\end{array} \longrightarrow \begin{array}{l}CH_3OC_6H_3O\\ \quad | \qquad\quad |\\ CH_3OC_6H_3CO\end{array}$$

According to this interpretation, the action of hydrogen peroxide on 3,6-dimethoxyphenanthrenequinone involves not only the usual splitting between the two ketone groups but also a cleavage of the bond between one ketone group and a benzene ring. So far as the author is aware, this type of oxidation has not been observed previously in the phenanthrenequinone series. It finds a certain parallel, however, in the alkaline oxidation of purpurin to 2,5-dihydroxybenzoquinone,[7] and a close analogy is found in the alkaline oxidation of alizarin to 2-hydroxy-1,4-naphthoquinone-3-vinylglyoxylic acid,[8] if it is true that this reaction involves, as the first step, the formation of a diquinone.

To return to the problem of determining the structures of the compounds listed in Table I, it will be seen that only the y- and the ζ-series remain to be accounted for. If it is again assumed that the second substituent enters the unsubstituted, terminal ring, only two structures remain for the y-series and two for the {-series: the γ-series must have the 3,5- or the 3,s-structure; the substituents in the {-derivatives must be in the 2,5- or the 2,8-positions. 2,5-Dihydroxyphenanthrenequinone, however, is a known compound,[9] and the dihydroxyphenanthrenequinone of the

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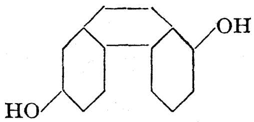
[7] Scholl and Dahll, *Ber.*, 57, 80 (1924).

[8] Scholl and Zinke, *ibid.*, 51, 1419 (1918).

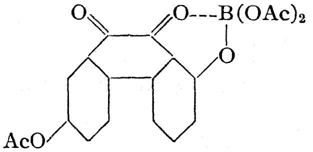
[9] Schmidt and Kampf, *ibid.*, 36, 3750 (1903), who first prepared this quinone, regarded it as 4,5-dihydroxyphenanthrenequinone, but the evidence of Christie and Kenner, J. Chem. *Soc.*, 470 (1926), and of Christie, Holderness and Kenner, *ibid.*, 671 (1926), convincingly supports the 2,5-structure.

ζ-series does not have the properties ascribed to this substance. It is probable, therefore, that the ζ-derivatives belong to the 2,8-series, X.

A very delicate means of confirming the structure assigned to the ζ-series, and of distinguishing between the two possible structures for the γ-compounds, was found in the application of the elegant method of Dimroth for the recognition of an hydroxyl group in a position adjacent to a quinone carbonyl group.[10] The method, which has been applied already to a few hydroxyphenanthrenequinones,[10b] consists in comparing the action of acetic anhydride on the quinone with the action of a solution of boro-acetic anhydride in acetic anhydride. With the latter reagent, ordinary acetylation takes place when the hydroxyl group is not adjacent to the carbonyl group, but an hydroxyl group in this favorable position, that is, in the 1- or &position in phenanthrenequinone, enters into the formation of a boro-acetate complex, which is characterized by having an intense color. Thus the quinone corresponding to X should yield the substance XI, and the formation of such a complex should be evident from the development of a distinctive color. With the absence of an hydroxyl group in the 1- or &position, both boro-acetic anhydride and acetic anhydride can be expected to yield a yellow or orange simple acetate.



X (ζ)

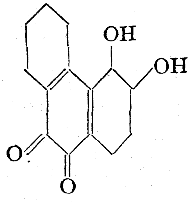


XI

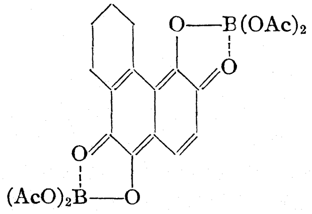
Before applying the Dirnroth test to the new dihydroxyphenanthrenequinones, it seemed desirable to extend Dimroth's observations by making at least a brief study of the action of the boro-acetic anhydride reagent on the various hydroxyphenanthrenequinones of known structure which have been prepared recently by the author. Experiment showed that the colors of the solutions in acetic anhydride and in the boro-acetic anhydride reagent were identical (usually pale yellow or orange) with quinones having the hydroxyl groups in the following positions: 2,5-, 2,6-, 2,7- and 3,6-, and to this list may be added, from Dimroth's results, the 2- and 3-derivatives. With the groups in the following positions, on the other hand, a striking change to green was observed in the presence of boro-acetic anhydride: 1,2-, 1,4-,[10b] 1,2,4-; while the color changed to red in the case of 1-hydroxyphenanthrenequinone, and 1,3,4-trihydroxy phenanthrenequinone gave a sparingly soluble red precipitate.

[10] (a) Dimroth and Faust, *Ber.*, **54**, 3020 (1921); (b) Dimroth, *Ann.*, **446**, 97 (1926); (c) Dimroth and Ruck, *ibid.*, **446**, 123 (1926); (d) Dimroth and Roos, *ibid.*, **456**, 177 (1927).

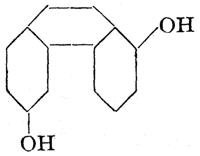
With only one compound was the behavior such as to constitute a possible anomaly. Morpholquinone, XII, though it contains no hydroxyl group in the favorable ortho position, imparts to a cold solution of boro-acetic anhydride a red color which becomes intensely purple on warming, and dark red crystals separate from the solution. On boiling, a deep green solution results. According to the theoretical analysis which Dimroth[10b] has made of the problem, it is possible that the formation of a complex is in this case due to a tautomeric change and that one of the products formed has the amphi-quinonoid structure, XIII, though the failure of 3-hydroxyphenanthrenequinone to form a complex renders this explanation unlikely. It is also possible that the two ortho hydroxyl groups enter into combination with the reagent, forming primary valence compounds of the type



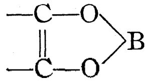
XII



XIII



XIV (γ)



$$\begin{matrix} —C—O \\ \| \\ —C—O \end{matrix}\!\!>\!B—OAc$$

, or complex compounds of the type described by Böesecken[11] and by Rosenheim and Vermehren.[12] A reaction of this character appears to be the more probable in view of the fact that the red precipitate first formed is not as easily attacked by water as the complexes obtained by Dimroth. Thus the present indications are that the unusual reaction of morpholquinone is connected with the presence of two adjacent hydroxyl groups. Since such a grouping is impossible for the two new dihydroxyphenanthrenequinones, it was felt that the test could be applied with confidence to these substances and the interesting behavior of morpholquinone was not studied further.

When the dihydroxyphenanthrenequinoneof the ζ-series was examined, it was found that boro-acetic anhydride produced an intense green coloration in the cold, and that this became purple on warming. The compound, therefore, has one group in the 1(or 8)-position and, since the other group is fixed at 2, and the compound differs from the known 1,2-isomer, the substance may be assigned the formula of the 2,8-derivative, corresponding to X. The isomer of the γ-series also forms a complex with boro-acetic anhydride, evident from the red coloration produced, and it is thus considered to be the 3,8-derivative, corresponding to XIV, though it is possible, if highly improbable, that it is 1,3-dihydroxyphenanthrenequinone.

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[11] Boesecken, Chem. Zentr., II, 1341 (1923).

[12] Rosenheim and Vermehren, *Ber.*, 57,1337, 1828 (1924).

The conclusions concerning the new dihydroxyphenanthrenes, and the disulfonic acids from which they were obtained, may be summarized in the following way

$$\text{Phenanthrene-3-sulfonic acid} \longrightarrow \begin{cases} \text{3,6-Disulfonic acid (a-Series)} \\ \text{3,7(or 2,6)-Disulfonic acid (8-Series)} \\ \text{3,8-Disulfonic acid } (\gamma\text{-Series}) \end{cases}$$

$$\text{Phenanthrene-2-sulfonic acid} \longrightarrow \begin{cases} \text{2,6-Disulfonic acid } (\delta\text{-Series}) \\ \text{2,7-Disulfonic acid } (\epsilon\text{-Series}) \\ \text{2,8-Disulfonic acid } (\zeta\text{-Series}) \end{cases}$$

In the monosulfonation of phenanthrene, the substituent enters the 1-, the 2-, the 3- and the 9-positions; a second substituent, at least in the case of the 2- and the 3-acid, enters the 8-, the 7- and the 6-, or what may be termed the 1′-, the 2′- and the 3′-, positions. In each case, the predominant isomer is that produced by substitution in the 3(or 6)-position. In no instance has substitution in the 4(or 5)-position been observed.

Experimental Part

Experiments with the Disulfonate Mixture.—It was stated in Part I that the neutralization of the sulfonation product with alkali causes the monosulfonates to crystallize out completely, while the disulfonates are largely retained in the mother liquor. When an attempt was made to isolate the disulfonic acids, in the form of their potassium salts, by concentration of such a solution, there separated at the boiling point a substance which appeared to be gelatinous, but which was found to have a fine, hair-like structure and to consist largely of potassium sulfate. The addition of a large quantity of potassium hydroxide, however, brings about the precipitation of a mixture of potassium phenanthrene-disulfonates. The material may be freed from inorganic salts by repeated precipitation with potassium hydroxide, followed by washing with alcohol, and analyses agreed with the values calculated for a disulfonate. The material is extremely soluble in cold water and it could not be crystallized. Even the barium salt is very soluble in water and has little tendency to crystallize; the solutions have a soapy consistency. The *p*-toluidine salt separates as an oil only from a very concentrated solution. By fusion of the disulfonate mixture and distillation of the product, a solid phenanthrol mixture was obtained but this is not well adapted to a separation by fractional crystallization. It is very readily soluble in alcohol and very sparingly soluble in benzene. Crystallization of the mixture obtained on acetylating this material gave some promise of success and this method of separation was adopted in the experiments described below.

The Sulfonation of Potassium Phenanthrene-3-sulfonate.—The sulfonates used in carrying out these reactions were carefully freed not only from all traces of isomers but also from traces of potassium chloride, which interferes with the reaction. Ninety-four grams of the potassium 3-sulfonate was stirred into 94 cc. of concentrated sulfuric acid and the mixture was heated in an oil-bath at 130°. The temperature of the reaction mixture soon reached 125°, and it was then maintained at 125–130° for one and one-half hours.[13] The reaction is exothermic and it is necessary to keep the bath temperature about 10° below that desired for the reaction. The mixture was stirred thoroughly in order to break up the lumps which first formed. A clear, viscous solution usually resulted after about thirty- minutes, and at the same time a crystalline salt began to

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[13] The results were the same when the heating was continued for three hours.

separate, so that, at the end of the specified time, a thick, almost solid, crystalline paste resulted. This was dissolved in 700–800 cc. of water and the solution was neutralized with a concentrated solution of about 200 g. of potassium hydroxide and then rendered slightly acid. The solution was next boiled down until the separation of solid material caused too much bumping, when it was poured, in portions, into an evaporating dish and dried in the oven.

The finely powdered mixture of disulfonates and potassium sulfate was fused with 700 g. of potassium hydroxide at a temperature of 280–305°. Fusion took place smoothly, giving a thick, brown melt. This was dissolved in water, to which ice was added, the greater part of the alkali was neutralized, and the hot, filtered solution was then acidified and cooled. The quality of the product was improved by a further precipitation from alkali, though the material slowly undergoes oxidation unless the solution is again acidified without delay. The dried phenanthrol mixture formed a gray powder weighing 55.5 g. and melting at about 175–200°. It was distilled at a pressure of 3 mm., taking care to avoid exposure of the molten material to the air, for it is easily oxidized. The distillate (51 g.) was dissolved in acetic anhydride and the solution was boiled for one hour and then poured into water. The diacetate mixture soon solidified and the crushed and well-washed material dried in the course of two days to a weight corresponding closely with the theoretical weight (71.3 g.). The product was somewhat green and melted at 95–125°.

The mixture of diacetates was first crystallized from a minimum quantity of alcohol in order to remove a small amount of acetic acid and oil, and then was subjected to a systematic fractionation from alcohol. The product at first separated in the form of a stiff paste of amorphous material, but, after six crystallizations, the top fraction formed blades of pure 3,6-diacetoxyphenanthrene (31.5 g.), while a further quantity (5 g.) of this isomer was soon separated as the least soluble of the remaining fractions. This isomer crystallizes in the form of long, flat blades having a characteristic gloss and melting, when perfectly pure, at 124.5'. On further crystallization the 3,8-isomer became concentrated in the top fraction along with the 3,6-derivative. For a time it was difficult to distinguish this mixture, which formed plates, from the pure 3'6-isomer, except that the melting point was a few degrees too low and not sharp. After further crystallization the melting point was raised to about 130°, at which point a fairly complete separation becomes possible. If a solution of the somewhat feathery plates is closely watched. a pause in the progress of the crystallization may be observed. If the solution is quickly filtered without undue disturbance, needles of the 3,8-isomer melting at 182–183° may be obtained, while blades of the nearly pure 3.6-isomer crystallize at once from the filtrate. Pure 3,8-diacetoxyphenanthrene forms long slender needles from alcohol and melts at 184°.

The 2,6-isomer becomes concentrated in the more soluble fractions and may be recognized from the fact that it forms clusters of stout needles melting at about 115–117". Though the crystals appear to be well-formed, the compound on further purification melts at 122–123° and forms small plates. The needle form, however, is not only characteristic of the material in a certain stage of purification, but it is an aid in effecting a separation. A mixture of these needles with blades of the 3,6-isomer may be warmed with alcohol until the blades are dissolved, without greatly affecting the compact needles.

While alcohol is preferred as a solvent with which to carry out the first crystallizations, a point is reached where further working of the mixture becomes unprofitable and it is then advisable to change to benzene–ligroin. Using the latter solvent, and having removed the greater part of the 3,6-isomer, it is found that the high-melting 3,8-diacetate is the first to crystallize. It first forms a crust of small crystals and then good, prismatic needles The 2'6-isomer again concentrates in the tail fractions and the 3,6-diacetate was obtained from intermediate fractions.

The separation was not carried to completion, but was interrupted when the following quantities of the pure isomers had been collected: 3,6-diacetoxyphenanthrene, 42.2 g.; 2,6-diacetoxyphenanthrene, 7.2 g.; 3,8-diacetoxyphenanthrene, 0.7 g.[14]

The Sulfonation of Sodium Phenanthrene-2-sulfonate.—A mixture of 63 g. of the salt and 63 cc. of concentrated sulfuric acid was heated at a temperature of 125–130° for just thirty minutes, when the reaction was found to be complete. The material in this case dissolved very easily and crystallization of the acid sodium salt did not take place. The reaction mixture was worked up and converted into a diacetate mixture in exactly the same manner as with the isomer. The crude phenanthrol mixture **(39.5** *g.)* gave 37.5 g. (71%) of distilled product, while the yield of the diicetate mixture was quantitative **(47.3** g.). The latter substance was somewhat oily until it was triturated with dilute sodium hydroxide solution.

The diacetate mixture was again fractionally crystallized from alcohol. On the first crystallization the material separated as an oil which soon solidified, but it thereafter formed crystals. After seven crystallizations, the greater part of the 2,6-diacetoxyphenanthrene was obtained from the top, or "less soluble," fractions (23 g.). The compound has been described above. The tendency to form needles when slightly impure was again noted.

2,7-Diacetoxyphenanthrene (m. p. 181.5") made its initial appearance in the very first mother liquor. The solution, which contained about one-fifth of the total product, was dark brown and contained ethyl acetate. On long standing it deposited hard crystalline clusters melting at about 120–140°. Once obtained in this condition, the diacetate was easily purified by crystallization from alcohol, for it now appears to be distinctly less soluble than either of the other isomers present. It forms small, thin plates when completely pure and when the solution cools slowly, though needle-like crystals were often obtained on rapidly cooling a solution.

The intermediate fractions, after the removal of small additional quantities of the 2,6-isomer, deposited a few of the hard clusters of the impure 2,7-diacetate, and the third isomer then made its appearance. 2,8-Diacetoxyphenanthrene first crystallized in the form of round clusters of needles radiating from a common base. The material had the appearance of a pure compound and melted fairly sharply at 117–118°, but after several crystallizations from alcohol and from benzene–ligroin, a constant melting point of 125" was found. The compound forms long slender needles from either solvent.

The amounts of the pure isomers which could be collected at a time were usually not over 0.1–0.2 g., and when the returns fell below this limit the solvent was changed. Before using benzene–ligroin, however, it seemed expedient to distil the collected material at a diminished pressure in order to remove moisture and some coloring matter. The glass-like product so obtained was caused to crystallize only by the use of alcohol, but it could then be crystallized from benzene–ligroin, From this solvent-pair, the 2,7-isomer separated first, followed by the 2,8-diacetate, while none of the 2,6-derivative could be collected.

The separation was discontinued when the following quantities of the pure isomers had been obtained: 2,6-diacetoxyphenanthrene, 25.6 *g.;* 2,7-diacetoxyphenanthrene, 1.0 *g.;* 2,8-diacetoxyphenanthrene, 0.5 g.

The 2,6-diacetoxyphenanthrene thus obtained was carefully compared with the product resulting from the sulfonation of phenanthrene-3-sulfonic acid, and the two substances, as well as their hydrolysis products and the dimethyl ethers, were found to be identical.

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[14] The presence of this last isomer was overlooked in earlier experiments carried out on a smaller scale.

Diacetoxyphenanthrenes.—Since each of the five isomers has been described in the foregoing passages, it is sufficient to record here the analyses.

TABLE II

DIACETOXYPHENANTHRENES, $C_{18}H_{14}O_4$

Positions of substituents	M. p., °C.	Appearance	Analyses, % C, calcd : 73.45	Analyses, % H, calcd.: 4.79
2,6	122–123	Plates	73.18	4.86
2,7	181.5 (183.5 corr.)	Plates	73.65	4.95
2,8	125	Needles	73.66	4.80
3,6	124.5	Blades	73 35	4.84
3,8	184 (186 corr.)	Needles	73.42	4.81

Dihydroxyphenanthrenes.—The diacetates were hydrolyzed by warming a suspension of the material in alcoholic sodium hydroxide solution. When the dissolution was complete, the solution was diluted with water and slowly acidified at the boiling point. The product then separated in a crystalline condition.

TABLE III

DIHYDROXYPHENANTHRENES, $C_{14}H_{10}O_2$

Positions of substituents	M. p., °C.	Appearance	Analyses. % C, calcd.: 79.98	Analyses. % H, calcd.: 4 80
2,6	234 (239, corr.)	Plates	79 82	4.91
2,7	258 (265, corr.)	Needles	79.65	4.90
2,8	202 (205, corr.)	Small needles	...	...
3,6	221 (225, corr.)	Large gray plates	79.69	4.77
3,8	247 (253, corr.)	Pink needles	80.06	4.88

The dihydroxyphenanthrenes are only sparingly soluble in toluene; they dissolve very readily in alcohol and they are moderately soluble in boiling water. They are conveniently crystallized from dilute alcohol or from a xylene–toluene mixture. No means was found for separating a mixture of isomers. The compounds may be distilled without loss if precautions are taken to avoid much contact of the molten material with the air. The specimens were colorless except as noted; attempts to remove the color in the cases of the last two compounds in the table were without avail. The dihydroxyphenanthrenes all form orange or yellow solutions in concentrated sulfuric acid. The alkaline solution exhibited a blue fluorescence with the 2,8-, the 3,6- and the 3,8-isomers, and all of the alkaline solutions slowly darkened on exposure to the air. Though it is theoretically possible to formulate quinones derivable from three of the compounds, none of the five isomers possesses the properties of a hydroquinone. 2,7-Dihydroxyphenanthrene, for example, might be expected to yield 2,7-phenanthrenequinone; but it is not attacked by silver oxide even in a boiling nitrobenzene solution. The other isomers are equally indifferent.

Dimethoxyphenanthrenes.—The ethers were prepared by methylation with dimethyl sulfate in alkaline solution. Their properties are all quite similar: they are very readily soluble in alcohol or benzene, and they form excellent, long, colorless needles on crystallization from methyl alcohol. In the case of the 2,6-isomer it is necessary to induce crystallization, best by seeding, for otherwise a sponge of amorphous material separates from the supersaturated solution. A mixture of benzene and ligroin is a less suitable solvent; with the 3.8-derivative, compact clusters of ill-formed crystals resulted. It is possible to effect a separation of mixtures of the isomeric ethers by fractional crystallization.

TABLE IV

DIMETHOXYPHENANTHRENES, $C_{16}H_{14}O_2$

Positions of substituents	M. p., °C.	Appearance	Analyses, % C, calcd.: 80.64	H, calcd.: 5.92
2,6	87	Needles	80.41	6.89
2,7	167–168	Needles	80.43	6.10
3,6	105	Needles	80.52	5.77
3,8	117	Needles	80.75	6.14

Diacetoxyphenanthrenequinones.—The conditions found most suitable for carrying out the oxidation of the diacetoxyphenanthrenes were as follows: 1 g. of the diacetate was dissolved in 8–10 cc. of glacial acetic acid and, while controlling the temperature to 60°, a solution of 1.1 g. of chromic acid in the minimum quantity of water, and diluted with glacial acetic acid, was added. A red solution resulted and in most cases it deposited the quinone, on cooling, in a crystalline condition. With the 2,7-isomer it was necessary to use more glacial acetic acid (19 cc.) in order to keep the diacetate in solution. The 2,8-isomer did not crystallize from the glacial acetic acid solution, and the addition of water caused the precipitation of an oil. When this was triturated with alcohol, a clean, solid product was obtained. With the other compounds it was only necessary to collect the crystalline material and to wash it thoroughly with alcohol, water, and again with alcohol, in order to obtain a good product. The yield, in the case of the 2,6-, 2,7- and 3,6-derivatives, was 0.5–0.7 g. of crystallized product, while the yield of the 2,8-isomer was much poorer. 3,8-Diacetoxyphenanthrenequinone was produced

TABLE V

DIACETOXY-9,10-PHENANTHRENEQUINONES, $C_{18}H_{12}O_6$

Positions of substituents	M. p., °C.	Appearance	Analyses, % C, calcd.: 66.65	H, calcd.: 3.73
2,6	216–217 (220–221 corr.)	Golden-yellow plates	66.42	3.80
2,7	238 (244 corr.)	Long slender orange needles	66.35	3.80
2,8	219–220 (223–224 corr.)	Orange plates	66.75	3.81
3,6	217 (232 corr.)	Fine yellow needles	66.39	4.01
3,8	217–218 (221–222 corr.)	Flat orange-yellow needles	66.43	3.82

in quantitative yield, which was a fortunate circumstance in view of the small amount of material available.

The isomers differ considerably in appearance and in their solubility relationships. The 2,6-derivative is moderately soluble in alcohol and crystallizes well from this solvent. With the 2,7- and the 3,6-derivatives, the solubility in alcohol is slight and the best solvent for the crystallization is glacial acetic acid. 2,8-Diacetoxyphenanthrenequinone dissolves readily in benzene and crystallizes well from a benzene–ligroin mixture. The 3,8-isomer gives a paste of poor crystals from glacial acetic acid but forms excellent crystals from alcohol or benzene. With all of the compounds several crystallizations are usually necessary before a pure product is obtained. Since the color reactions of these quinones are reactions characteristic of their hydrolysis products, they will be described below.

Dihydroxyphenanthrenequinones.—The diacetoxyphenanthrenequinones were hydrolyzed with alcoholic sodium hydroxide solution. The reaction proceeds in the cold, with the formation of an intensely colored solution, and a sodium salt soon begins to precipitate. The mixture is diluted with water and heated until all of the material passes into solution, and the filtered solution is acidified. The product often separates in a highly dispersed condition, but it becomes more easily filterable on digestion at the boiling point. A very good product was obtained in each case. Only two of the isomers were available in quantity sufficient for analysis.

2,6-Dihydroxyphenanthrenequinone.—While no solvent suitable for the crystallization of this material was found, the reprecipitated material gave satisfactory analytical figures. It was obtained as a reddish-brown powder, readily soluble in glacial acetic acid or alcohol, very sparingly soluble in xylene and rather hygroscopic. It is easily acetylated by acetic anhydride in conjunction with either pyridine or concentrated sulfuric acid.

Anal. Calcd. for $C_{14}H_8O_4$: C, 69.99; H, 3.36. Found: C, 69.88; H, 3.56.

3,6-Dihydroxyphenanthrenequinone.—As precipitated from an alkaline solution, the material formed a light orange powder. It is very sparingly soluble in water, alcohol or glacial acetic acid, and only moderately soluble in nitrobenzene. Crystallization from the latter solvent gave orange-red micro-needles

Anal. Calcd. for $C_{14}H_8O_4$: C, 69.99; H, 3.36. Found: C, 69.81; H, 3.81.

An account of the color reactions of the five dihydroxyphenanthrenequinones is given in Table VI, while Table VII summarizes a series of

TABLE VI

COLOR REACTIONS OF THE DIHYDROXYPHENANTHRENEQUINONES

Positions of substituents	Color	Color of the solution in			
		H_2SO_4	0 1 N NaOH	6 N NaOH	Pyridine
2,6	Brown-red	Yellow-green	Red	Intense red	Orange
2,7	Dull red	Brown	Green	Yellow	Red
2,8	Dull red	Green	Intense purple	Purple	Red
3,6	Orange	Red	Red	Red	Orange-yellow
3,8	Red	Pale purple	Light red	Light red	Yellow

tests in which the action on the quinones of acetic anhydride and of boro-acetic anhydride is compared. The latter reagent consisted of a solution of 0.5 g. of pyroboro-acetate[10] in 10 cc. of acetic anhydride. In those cases in which the color of the solution changes on warming, the color of the solution at about 25" and at about 60" has been noted.

TABLE VII

THE ACTION OF BORO-ACETIC ANHYDRIDE ON HYDROXYPHENANTHRENEQUINONES

Positions of substituents	Color of the solutions (25 to 60°) in	
	Acetic anhydride	Boro-acetic anhydride
1	Yellow	Red
1,2	Red to orange	Green to red
3,4	Pale orange	Red to purple[15]
2,5	Pale red to orange	Pale red to orange
2,6	Yellow	Yellow
2,7	Yellow	Yellow
2,8	Pink to orange-yellow	Chrome-green to purple
3,6	Yellow	Yellow
3,8	Yellow	Red
1,2,4	Faint purple to yellow	Green to red
1,3,4	Red to yellow	Red[16]

Comparison of ε-Diacetoxyphenanthrenequinone with 2,7-Diacetoxyphenanthrenequinone.—Since the ε-quinone, which, for convenience, has been called 2,7-diacetoxyphenanthrenequinone in the above passages. corresponded closely in properties with the substance known to have this structure,[3] a direct comparison was desirable This was greatly facilitated by Professor Brass, who kindly supplied a sample of the material, in an impure condition. After repeated crystallization from glacial acetic acid, the substance formed brown-red lumps of indefinite shape and the melting point was raised to 234°. The sample obtained in the present work had an entirely different appearance (long, orange needles) and melted at 238°, but mixtures of the two specimens always melted between these two temperatures. After assuring myself that other diacetoxyphenanthrenequinones which melt at about the same temperature exhibit a very decided depression when mixed with each other, I became convinced that the two specimens were identical, but that the material prepared from the diacetoxyphenanthrene was purer than that previously obtained. This conclusion was supported by the results of comparative color tests with the dihydroxyphenanthrenequinones obtained by hydrolyzing the two diacetates. The new compound, as precipitated from an alcoholic alkaline solution, has a dull blue color under certain lighting conditions, but the true color, clearly seen on rubbing the material on a glass slide, is dull red. The microscope revealed a mass of well-formed needles. The compound of known structure, which may be called the Anschiitz compound, after the discoverer, was also dull red when rubbed on glass but the crystalline structure was not well developed. The most characteristic color reaction of the Anschiitz compound, as described by Werner,[3c] is that the yellow-green solution in very dilute alkali becomes yellow on adding more concentrated alkali. Table VI shows that the present compound likewise gives this test. The only difference observed in a direct comparison was that the solutions of the Anschiitz compound were less bright than the others, and this was true of the solutions in concentrated sulfuric

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[15] Dark red crystals separated on gently heating; the solution became brown and then intensely green on boiling.

[16] Dark red crystals were deposited.

acid and in pyridine. All of these observations indicate the identity of the two compounds and show that the method of preparation here described yields a better product than has yet been obtained by the older method of hydrolyzing the tetrazonium salt of 2,7-diaminophenanthrenequinone.

Proof of the Structure of the α-(3,6)-Dihydroxyphenanthrene

3,6-Dimethoxyphenanthrenequinone.—Thirty-two grams of 3,6-diacetoxyphenanthrene was hydrolyzed with alcoholic sodium hydroxide solution and the product was methylated with dimethyl sulfate in alkaline solution. The ether was purified by distillation at a pressure of 3 mm., when it melted at 102°; yield, 25 g. (96%). This material was dissolved in 170 cc. of glacial acetic acid, the solution was cooled to 60° and a solution of 27 g. of chromic acid was slowly added while the temperature was kept below 70° by cooling in an ice-bath. In the early stages of the reaction a tarry brown precipitate formed, but this soon dissolved and crystals of the quinone were deposited from a dark red solution. On completion of the reaction the solution was well cooled and the product was collected and washed with alcohol. A single crystallization from glacial acetic acid gave a pure product; yield, 16.2 g. (60%).

The quinone is sparingly soluble in alcohol and only moderately soluble in glacial acetic acid. It crystallizes well from the latter solvent, forming yellow needles melting at 235" (241° corr.).

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.62; H, 4.51. Found: C, 71.36; H, 4.46.

Oxidation of **3,6-Dimethoxyphenanthrenequinone.**—A solution of 9 g. of this quinone in 450 cc. of glacial acetic acid was prepared and cooled to 90°. Six cc. of 30% hydrogen peroxide solution was then added and the solution was allowed to stand at 60–90° for two hours. Part of the quinone had crystallized at the end of this time; this was dissolved and the solution was again treated with 6 cc. of hydrogen peroxide solution. While the quinone did not again separate, it was found advisable to repeat this process after a further two hours and then to allow the solution to stand in a warm place overnight. The greater part of the acetic acid was then removed from the pale brown solution by distillation and water was added. This caused the separation of a dark brown oil, but this partially dissolved and partly solidified on adding an excess of alkali. After prolonged boiling the solid was all brought into solution, but the solution had such a dark brown color that it was treated with a little hydrogen peroxide and warmed until it become pale yellow.[17] The yellow product which precipitated on acidifying the solution, and after very thorough cooling, was triturated with a cold, dilute sodium carbonate solution until no more material dissolved. The residue was only slightly colored, and it was found to consist of the lactone described below in nearly pure form; yield, 0.9 g.; m. p. 190°. From the carbonate solution there was obtained 3.6 g. of 5,5′-dimethoxydiphenic acid, which was somewhat yellow, but fairly pure.

5,5′-Dimethoxydiphenic Acid (V).—Like the parent acid, this substance has a pronounced tendency to form supersaturated solutions. It dissolves very readily in alcohol or glacial acetic acid, moderately in water and is practically insoluble in benzene. The crude material was crystallized several times from dilute alcohol and then from methyl alcohol, when it was obtained in the form of colorless needles melting at 229" (234° corr.).

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.56; H, 4.67. Found: C, 63.27; H, 4.69.

1,6-Dimethoxyfluorenone-4-carboxylic Acid.—The dimethoxydiphenic acid forms a brown solution in concentrated sulfuric acid which rapidly becomes deep red on warming. Such a solution was warmed at about 50° for one-half hour and then poured into

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[17] The results were the same when this treatment was omitted, or when the crude oil was first treated with carbonate solution.

water.* This caused the separation of a finely divided yellow substance. The compound is only moderately soluble in glacial acetic acid, but it forms good, small, bright yellow crystals if the solution is cooled rapidly or seeded; otherwise an amorphous product slowly separates from a highly supersaturated solution. The compound decomposes alkali carbonates; it melts at 295° (303° corr.) and gives off carbon dioxide at that temperature,

Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.59; H, 4.26. Found: C, 67.32; H, 4.28.

For further characterization the fluorenonecarboxylic acid was converted into ***the amide,*** as follows: 1.2 g. of the acid was heated with 1 g. of phosphorus pentachloride at 130° until most of the phosphorus oxychloride had been removed. The crude acid chloride was dissolved in benzene, the solution was filtered from a small amount of the unchanged acid, and treated with dry ammonia. A heavy precipitate of the amide soon separated. This was triturated with dilute ammonia solution and crystallized from glacial acetic acid. Rapid cooling was again necessary for the production of good crystals as small, yellow needles, 0.6 g.; m. p. 261° (268° corr.).

Anal. Calcd. for $C_{16}H_{13}O_4N$: C, 67.83; H, 4.63. Found: C, 67.66; H, 4.97.

The Synthesis of **5,5'-Dimethoxydiphenic Acid.**—4-Methoxy-2-aminobenzoic acid was prepared according to the excellent directions of Ullmann and Dootson,[18] starting with *p*-toluidine, and the diazonium salt was reduced with an ammoniacal solution of cuprous hydroxide according to the general method of Vorländer and Meyer.[19] A cuprous hydroxide solution was prepared by adding a solution of 2.7 g. of hydroxylamine hydrochloride and 6.5 cc. of 6 N sodium hydroxide to a solution of 6.3 g. of copper sulfate and 7.5 cc. of concentrated ammonia water in 30 cc. of water. A suspension of 1.7 g. of 4-methoxy-2-aminobenzoic acid in 1.8 cc. of glacial acetic acid and 4 cc. of water was diazotized with a solution of 0.7 g. of sodium nitrite. The amine dissolved slowly on shaking the mixture, but a small amount of the azo compound was produced. The filtered solution of the diazotized amine was added in small portions to the well-cooled cuprous hydroxide solution, each portion producing a green foam which soon dissolved. The dark yellow-green solution became pale yellow on warming to the boiling point, when it was made acid to Congo Red paper and cooled well. The product, which contained much copper salt, was digested with sodium carbonate solution and the crude dimethoxydiphenic acid was recovered on acidifying the filtered solution.

The product was quite yellow, melted at about 190° and was only obtained in a pure condition after numerous crystallizations from methyl alcohol. It then formed colorless needles melting at 228°.

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.56; H, 4.67. Found: C, 63.70; H, 4.63.

Mixtures of this acid with the acid, m. p. 229°, obtained from 3,6-dimethoxyphenanthrenequinone showed no depression in the melting point. The identity of the two substances was further confirmed by the conversion of the synthetic acid into 1,6-dimethoxyfluoreneone-4-carboxylic acid, which was found to melt at 295° and to be identical with the material already described.

Lactone of **1-Hydroxy-4,4'-dimethoxydiphenyl-1'-carboxylic** Acid **(VII).**—The carbonate-insoluble product resulting from the oxidation of 3,6-dimethoxyphenanthrenequinone was easily purified by crystallization from alcohol, in which it is moderately soluble, and from which it separates in the form of long, colorless needles melting at 191° (194° corr.).

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72. Found: C, 70.21, 70.12; H, 4.67, 4.56.

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[18] Ullmann and Dootsou, ***Ber.***, 51, 19 (1918).

[19] Vorliinder and Meyer, *Ann.*, 320,122 (1902).

The substance may be distilled without decomposition. The crystalline material dissolves only very slowly on boiling with alkali, though the resulting salt is very readily soluble in water. On acidifying the solution, even at a low temperature, the lactone and not the free acid results.

Since it is conceivable that the lactone is formed not from the dimethoxyquinone but from the dimethoxydiphenic acid, the latter compound was subjected to the action of hydrogen peroxide in glacial acetic acid solution; in no case was a trace of the lactone obtained, and the greater part of the dimethoxydiphenic acid could be recovered after the prolonged action of a large excess of hydrogen peroxide.

1,4,4′-Trimethoxydiphenyl-1′-carboxylic Acid (VIII).—This was produced by shaking an alkaline solution of the above lactone with dimethyl sulfate until a precipitate began to separate from the alkaline solution. The solution, which was kept strongly alkaline, was then boiled until traces of the ester were hydrolyzed and then acidified. An oily product separated and soon solidified. This was precipitated from a carbonate solution and then crystallized from alcohol and from benzene–ligroin. It formed small, colorless prisms melting at 147–148°.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.65; H, 5.60. Found: C, 66.57; H, 5.42.

1,4,6-Trimethoxyfluorenone (a).—The above acid dissolved in cold concentrated sulfuric acid to give an intensely crimson solution. After ten minutes the solution was poured into water, when an orange oil resulted. This soon changed to a yellow solid. It was washed with dilute alkali and crystallized from alcohol. It dissolves readily in this solvent and separates in the form of light clusters of small yellow needles melting at 157°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.09; H, 5.22. Found: C, 70.97; H, 4.85.

Summary

In order to gain an idea of the composition of the mixture of disulfonates which is produced by the action of sulfuric acid on phenanthrene, two of the pure monosulfonic acids were sulfonated and the products were at least partly identified by separating the mixtures of diacetoxyphenanthrenes which were obtained as the result of alkali fusion and acetylation. Derivatives of five new dihydroxyphenanthrenes were thus obtained, and it was possible to determine the structures of all of these compounds. From the results of this study, it was concluded that, when either the 2- or the 3-sulfonic acid derivative of phenanthrene is sulfonated, the second substituent enters the unsubstituted, terminal nucleus in the 6-, the 7- and the 8-positions.

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[CONTRIBUTION FBOM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

THE MELTING POINTS OF NORMAL PARAFFINS

BY J. H. HILDEBRAND AND A. WACHTER

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In connection with a study of the solubility relations of dicetyl which we are making, it became necessary to have a reliable value for the melting point of the substance. The value given in "International Critical Tables" is 75°, whereas our own material, synthesized according to the method of Sorabji,[1] purified by recrystallization four times from glacial acetic acid and then four times from benzene, gave a melting point of 70.2°. The last crystallization made no change in the melting point. The determinations were made by the aid of a standardized thermometer properly corrected.

A search of the original sources showed the following values, arranged in chronological order: 70,[1] 70.0,[2a] 68–70,[3] 69.8,[2b] 71,[4] 70,[5] 70.5,[6a] 74–75[7] and 70.5°.[6b]

These values all fall in the neighborhood of 70°, with the exception of the one by Levene, West and van der Scheer. It seemed rather surprising that the expert should have chosen for the tables a single value so divergent from all the others. We accordingly sought a further check, as follows. The normal paraffins might be expected to have melting points increasing regularly with molecular weight, for any differences in crystal form cannot involve much difference in energy with such soft substances as these. We accordingly plotted the melting points of the series from $C_{19}H_{40}$ to $C_{38}H_{78}$ against the number of carbon atoms, as shown in Fig. 1. The points are derived from the references already given. It will be seen that all the points fall rather close to a smooth curve excepting those of Levene, West and van der Scheer, for seven members of the series, these falling from 3 to 5° above the curve. In view of the concordance existing among practically all of the other data, we believe that the figures of these three collaborators should have been rejected instead of selected for "International Critical Tables." Since the curve we have drawn appears to express the other data satisfactorily, except for experimental uncertainties, we suggest the following temperatures read from it as the best values for the melting points of the normal paraffin hydrocarbons from $C_{19}H_{40}$ to $C_{36}H_{74}$.

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[1] Sorabji, J. *Chem. Soc.*, 47, 39 (1885).

[2] Krafft, (a) *Ber.*, 19,2219 (1886); (b) ibid., 40,4783 (1907).

[3] Mabery, THIS JOURNAL, 27, R35 (1905).

[4] Meyer and Soyka, *Monatsh.*, 34, 1163 (1913).

[5] Spath, *ibid.*, 34, 1987 (1913).

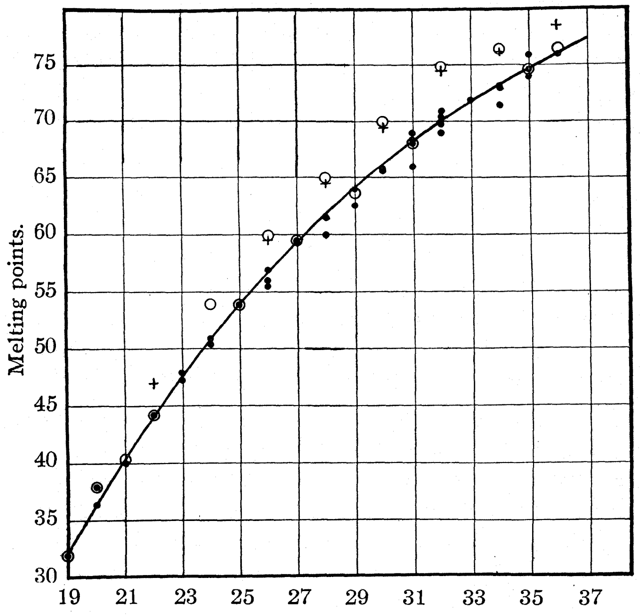
[6] Gascard, (a) *Compt.* rend., 159,258 (1914); (b) J. *Chem. Soc.*, *106*, 1045 (1914); *(c) Ann. china.*, 15,332 (1921).

[7] Levene, West and van der Scheer, *J. Biol. Chem.*, 20,521 (1915).

No. of carbon atoms	19	20	21	22	23	24	25	26	27
M. p., °C.	32	36.5	40.5	44	47.5	51	54	57	59.5

No. of carbon atoms	28	29	30	31	32	33	34	35	36
M. p., °C.	62	64	66	68	70	72	73.5	75	76

It will be seen from the figure that there is no real evidence for any alternation between the melting points of the even and odd members of the series in the range here considered, although it exists for the lower members up to about $C_{15}H_{32}$.[8]



⊙, "International Critical Tables;" ●, various sources; +, Levene, West and van der Scheer.

Fig. 1.

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[8] Cf. Tsakolotos, *Compt. rend.*, 143, 1235 (1900).

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL RESEARCH OF THE PENNSYLVANIA STATE COLLEGE]

THE VAPOR PHASE HYDROLYSIS OF PHENYL CHLORIDE AND BROMIDE

BY LYMAN CHALKLEY, JR.[1]

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Introductory

Meyer and Bergius in their excellent work upon the hydrolysis of the phenyl halides[2] record an experiment in which water and phenyl chloride were heated under pressure to 300°. A trace of phenol was obtained. Except for this result there appears to be no mention in the literature of the possibility of effecting the hydrolysis of phenyl halides with water alone.

In the course of a search for new methods for the synthesis of phenol, the direct hydrolysis of phenyl chloride with water alone in the vapor phase was attempted and, rather surprisingly, found to be possible. In a preliminary experiment a few grams of chlorobenzene and water were passed at atmospheric pressure through a little silica gel heated to 500°. Phenol and acid were formed.

There was not available sufficient information in regard to the free energy changes involved to permit the calculation of the equilibrium at 500° in the reaction $C_6H_5Cl + H_2O = C_6H_5OH + HCl$. Yet before proceeding further it was desirable to know at least whether or not the equilibrium was such as to greatly favor the presence of phenyl chloride in the equilibrium mixture.

Therefore a preliminary attempt was made to reverse the original reaction. Hydrogen chloride and phenol were passed through silica gel heated to 500°. Phenol was recovered, and, except for a little discoloration, appeared to be pure. It crystallized at room temperature and was completely soluble in sodium hydroxide solution. No trace of phenyl chloride was found.

As these experiments indicated that the vapor-phase hydrolysis of phenyl chloride was, at least, an interesting possibility, the work reported in this paper was carried out.

This investigation was designed essentially as a first exploration of the field. After the work here reported was completed, a notice appeared of the filing of an English patent application[3] which seemed to indicate that the present line of experiment had already been anticipated in Germany; but since a detailed discussion of the German invention will probably not

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[1] Bakelite Corporation Fellow.

[2] Kurt Meyer and F. Bergius, *Ber.*, **47**, 3155–3160 (1914).

[3] I. G. Application No. 10206 of April 4, 1928, Convention date April 6, 1927. Illus. Official J., 2054, 2149 (May 31, 1928).

be available for some years, the results of the present investigation are published with the idea that they may be of immediate interest.

My results indicate that at 300° and above chlorobenzene and bromobenzene can be hydrolyzed by water in the presence of a variety of catalysts. At temperatures around 500° the reaction is quite rapid. Phenol, the halogen acid and diphenyl ether appear to be the chief products. Silica gel, titania, thoria, zirconia, alumina and the blue oxide of tungsten were found to bring about the hydrolysis. The only catalyst that was tried which proved to be relatively inactive was a sample of kaolin. Titania and silica gel appear to be the most active.

Under the conditions of the experiments as they were carried out **it** proved easy to hydrolyze from 25 to 40% of the phenyl halide in one passage over the catalyst. The unhydrolyzed halide was recovered unchanged.

Experimental

Apparatus.—The apparatus used was the simplest that could be devised and consisted of a reservoir in which water and the phenyl halide were vaporized, a reaction tube which held the catalyst and was heated by a furnace and a receiver in which the products of the reaction were collected.

The reservoir was a 250-cc. distilling flask. In this were placed both the water and the phenyl halide, and the two were vaporized together, *i. e.*, the phenyl halide was steam distilled from the distilling flask. The vapor was passed through the catalyst held in a 1-meter pyrex tube having an inside diameter of about 2 cm. and heated by *a* 12-inch Hoskins' tube furnace. The lower end of the reaction tube was introduced directly into the mouth of a receiving flask in which the reaction products accumulated.

The side arm of the distilling flask reservoir was bent so that it would pass directly into the reaction tube when the latter was held in a vertical position. The gas-tight connection between the side arm of the distilling flask and the reaction tube was made with a rubber stopper. It was necessary to renew this stopper occasionally because of the disintegrating effect of the phenyl halides on the rubber.

Within the reaction tube the catalyst was supported on a spiral of pyrex glass rod, which was in turn held by a constriction in the reaction tube itself. **A** little pure shredded asbestos was usually placed on the glass spiral and the catalyst poured upon the asbestos. Fifty cc., the amount of silica gel used, filled 18 to 20 cm. of the tube. On top of the catalyst was placed sufficient shredded asbestos to fill the tube to above the region covered by the furnace. This asbestos filling was necessary to prevent drops of liquid which condensed in the side arm of the distilling flask from falling directly into the heated portion of the tube. The asbestos layer retained 1 to **3** g. of the reaction mixture.

The temperature of the furnace was determined and regulated by means of a thermocouple and a Brown control pyrometer, The thermocouple was placed in the furnace between the reaction tube and the furnace wall. Therefore, the temperature recorded was that of the furnace rather than that of the catalyst. However, with a not too rapid flow of gas the two temperatures do not differ greatly.

The reaction tube was connected with the receiving flask by means of a rubber stopper. **A** small glass tube which also passed through the rubber stopper provided an **air** vent. In a number of experiments this vent was connected with a wet test gas meter. In no case where the catalyst was heated to less than 700" was there any evidence of the evolution of gas. Of course, hydrogen halides would not show up on the dial of the gas meter, but in only one or two experiments war the reaction product saturated with halogen acid.

In the two experiments in which the catalyst was heated to above the melting point of pyrex, the glass reaction tube was replaced by a 3-ft. length of standard $^1/_4$-inch "Ambrac" pipe. This is a copper alloy containing approximately 75% of copper, 20% of nickel and 5% of zinc. The silica gel was supported in the Ambrac pipe on a spiral of copper wire.

Materials.—The first experiments were performed with Kahlbaurn's chlorobenzene. In later work this was replaced by Eastman "practical" chlorobenzene. Both Kahlbaum's and the pure grade of Eastman bromobenzene were used and no difference was noticed in their behavior.

The silica gel employed as catalyst was 8- to 14-mesh material obtained from the Silica Gel Corporation. The other catalysts were prepared in the laboratory.

Preparation of Catalysts.—Zirconia was prepared by precipitation with ammonium hydroxide from a solution of 100 g. of zirconium nitrate (Rahlbaum) in 500 cc. of water. The precipitate was washed by decantation, collected on a filter and dried at 195°.

Aluminum hydroxide was precipitated with ammonia from a solution of 300 g. of aluminum nitrate in a liter of water. The product was collected on a filter, partially dried at 195° and dried further in the reaction tube.

Ammonium tungstate (75 g.) was dissolved in a solution of 25 g. of sodium hydroxide in 500 cc. of water. Tungsten oxide was precipitated from this solution by the addition of 100 cc. of hydrochloric acid. The precipitate was collected on a filter, dried overnight at 195°, then washed repeatedly with water and again dried at 195°. The yellow oxide so produced was reduced in the reaction tube to the blue oxide. In Expt. 9, listed below, the reduction was carried out with formicacid. In Expt. 10 the reduction was effected with alcohol.

The thoria catalyst was prepared as follotvs: 22.3 g. of thorium oxalate was dissolved in a solution of 50 g. of ammonium bicarbonate in 350 cc. of water and the solution was evaporated on 60 cc. (30 g.) of granulated pumice. The product was dried at 130° and the thorium salt decomposed to thoria by heating in the reaction tube.

To prepare the titanium catalyst 100 g. of anhydrous titanium tetrachloride was poured into one liter of water and the mixture made alkaline with ammonium hydroxide. The product when dried at 195° was an orange-colored powder.

Operation.—In the performance of the experiments the catalyst was first charged into the reaction tube. The quantity of silica gel used was always 50 cc. when the glass reaction tube was employed. Fifty cc. of the thoria catalyst on pumice was also used. With the other catalysts, however, the effective volumes varied; and, as they actually changed in the reaction tuhe, these volumes were not constant and were usually less than 50 cc.

Known quantities of water and of the phenyl halide under investigation were placed in the distilling flask along with some chips of unglazed porcelain. The distilling flask with its contents was then weighed and connected with the reaction tube.

When the reaction tube was heated to the temperature at which the experiment was to be run, the mixture of water and phenyl halide was slowly distilled by means of a gas flame. As the gas supply was quite irregular, the rate of distillation varied from one experiment to another, and constituted the least controlled factor in the experiments.

At the conclusion of an experiment the distilling flask was again weighed with its contents. The receiving flask with the reaction products was also weighed. The weights of the materials entering into the reaction, and the materials recovered never differed by more than 3 g. This difference was accounted for largely, if not completely, by the liquid held on the asbestos packing in the reaction tuhe.

The reaction product was separated into its two components, an aqueous layer and an oily layer. The weights and volumes of these layers were determined, and a portion of the aqueous layer was titrated with $N/10$ potassium hydroxide. From this titration the quantity of acid liberated in the hydrolysis was determined. The small amount of acid dissolved in the oily layer was neglected. That the acid formed was actually hydrochloric or hydrobromic was determined in several cases by the precipitation of the silver halide.

In a number of experiments the reaction product was distilled; but as no efficient micro-fractionating column was available, distillation did not provide a satisfactory method for the determination of phenol. However, distillation did demonstrate the presence of diphenyl ether. A quantitative determination of this substance was not attempted.

Phenol was determined by the following procedure. The oily layer of the reaction product (or its distillation products) was extracted with 20% sodium hydroxide solution, the extract combined with the aqueous layer of the reaction product, the whole neutralized with hydrochloric acid, filtered, treated with excess of bromine water and the precipitated tribromophenol bromide dried and weighed. This method is not altogether satisfactory but is sufficiently accurate for the work here considered.

That the product of the hydrolysis was actually phenol was shown by the reduction of some of the tribromophenol bromide with sodium acid sulfite and comparison of the melting points of the tribromophenol so formed and of a mixture of this tribromophenol with Kahlbaum's tribromophenol.

When Eastman "practical" chlorobenzene was used small quantities of a difficultly water-soluble phenol were formed. The presence of this little-soluble phenol was shown by the fact that when the alkaline extract of a hydrolysis product prepared from "practical" chlorobenzene was neutralized the solution became cloudy. This behavior suggests that chlorophenol may have been formed from small quantities of dichlorobenzene present in the "practical" chlorobenzene used. This phenomenon was not observed when the purest grade of chlorobenzene and bromobenzene was used.

Results

In Table I are shown in considerable detail the data from eight experiments in which silica gel was used as the catalyst. Kahlbaum's chlorobenzene was used in Expts. 1 and 2. Eastman bromobenzene was used in Expts. 3, 4 and 5. Eastman "practical" chlorobenzene was used in Expts. 6, 7 and 8.

In Expts. 1 to 6, inclusive, the temperature of the furnace was 500°. In Expt. 7 it was 550° and in Expt. 8 it was 600°.

The same silica gel was used in Expts. 1 and 2. A fresh sample was used for Expt. 3 and this sample was left in the tube and used also for Expts. 4 and 5. However, between Expts. 4 and 5 the reaction tube with the catalyst in it was heated to 600° for an hour while a stream of air was blown through. A fresh sample of catalyst was used for Expt. 6. This was retained in the reaction tube for Expts. 6, 7 and 8, but was heated to 600° in air after each experiment. The silica gel darkens with use but the heating in air burns off the coloring matter and restores the gel to its original light color. The results show that it also restores the catalytic activity,

In Table II are shown the results obtained with other catalysts, and with

TABLE I

DATA USING SILICA GEL

No.	Duration, hrs.	Temp., °C.	Halide	Materials Phenyl halide, g.	Materials Water, g.	Rate of flow of react. mixt. Phenyl halide, g./hr.	Rate of flow of react. mixt. Water, g./hr.	Products Total, g.	Products Oil layer, g.	Products Water layer, g.	Products Water layer, cc.
1	2	500	Cl	75	32	37	16	104.5	74.5	30	30
2	0.5	500	Cl	23.4	10	46	16	31	23	8	8
3	2.5	500	Br	30	21	12	8.4	48	28.5	19.5	19
4	2.5	500	Br	34	22	13.6	8.8	53.5	30	23	20
5	0.5	500	Br	6		12		7.5	4		
6	17 min.	500	Cl	47	19	165	67	61.5	44	16	16
7	1.5	550	Cl	23	10	15.4	6.7	30	18.5	11	9
8	1.75	600	Cl	34	14	19.5	8	46	28.5	17	15

No.	Wt. diff. reactants and prods., g.	Water layer, *N*	Hydrolysis, %	Residue above 190° (uncorr.), g.	Phenol weighed as tribromophenol bromide g.	Phenol based on amt. of hydrolysis, %
1	2.5	2.34	10.5	0.5	4.45	68.5
2	2.5	1.8	7	..	..	..
3	3	2.66	26.5	1.5	2.7	57
4	0.5	1.44	13.3	..	..	..
5	..	4.05	43	..	0.246	21
6	4.5	1.02	3.3	..	..	..
7	3	8.63	38	..	3.85	53
8	2	7.7	38.2	1.5	5.25	49

silica gel at low and high temperatures. In this table the quantity of acid formed is given alone as being the most accurate index of hydrolysis (except when the metal tube was used). Fresh samples of catalyst were employed for each of the experiments 9 to 16, inclusive, and for 21. In the low-temperature experiments (16 to 20) there was practically no fouling of the catalyst and, therefore, fresh catalyst was not needed. As the silica gel used contained a trace of acid it was necessary to wash it with steam until the condensate was neutral before beginning the experiments. Between Expts. 21 and 22 the silica gel was heated in air to 845° for fifteen minutes.

Discussion

The experiments recorded in Table I show that phenyl chloride and phenyl bromide are readily hydrolyzed by steam when passed over silica gel at 500 to 600°. If Expts. 1, 2 and 6 are compared it will be seen that the amount of hydrolysis increases as the rate of flow of the reaction mixture over the silica gel is diminished. There is, therefore, no reason to believe that equilibrium in the hydrolysis of phenyl chloride was reached in the experiments. It is probable that the reaction mixture of phenyl chloride and steam of the composition used would undergo a greater hydrolysis than 10% at 500° if its contact with the catalyst were prolonged.

TABLE II

RESULTS WITH OTHER CATALYSTS

No.	Catalyst	Temp., °C.	Dur. of run, min.	Total wt. of prods., g.	Aq. layer, cc	Acidity of aq. layer, $N/10$	Hydrolysis %
9	Blue tungsten oxide	500	30	Product alkaline from NH_3			
10	Blue tungsten oxide	500	30	28.5	7	1.88	0.73
11	ZrO_2	500	30	46	12	6.9	2 9
12	Al_2O_3	530	60	29	7 5	5.1	2.3
13	ThO_2	500	45	42 5	11	4 2	1 7
14	Kaolin	500	30	16	3	0 07	0.02
15	TiO_2	500	30	33.5	10	20 0	10.0
16"	SiO_2	260	30	5	. .	0.05	. .
17[b]	SiO_2	300	30	. .		04	. .
18	SiO_2	350	30	13	. .	1 11	
19	SiO_2	400	30	16 5	. .	4 45	
20[c]	SiO_2	300	30	22.5	. .	0.36	. .
21	SiO_2	800	15	19	. .	13.3	. .
22	SiO_2	500	Short run indicated acid and phenol formed in quantity				

The formation of phenol was demonstrated in all experiments except No. 14.

[a] Faint trace of phenol. [b] Trace of phenol. [c] Phenol present.

At this same temperature, 500°, phenyl bromide hydrolyzes more completely than phenyl chloride under the conditions of the experiments. However, the phenyl bromide reaction mixture contained a higher molecular proportion of water than the phenyl chloride reaction mixture, and it was possible to pass the phenyl bromide over the catalyst at a slower rate.

At 550 and 600° phenyl chloride was found to hydrolyze to the extent of 38% under the conditions of the experiments.

In the last column of Table I are shown the yields of phenol obtained. The calculated yields of phenol corresponding to the halogen acid found are taken as 100%, and the figures given in the last column of Table I were computed on this basis. That is, for instance, the phenol found in Expt. 1 was 68.5% of 10.5% of the phenyl chloride used. The actual gross yield of phenol in Expt. 1 was about 7% of the phenyl chloride passed over the catalyst.

As already mentioned, the figures given for phenol yields are not very accurate, and that given for Expt. 5 is particularly questionable because of the small quantity of materials used in the reaction. However, it is safe to conclude that the chief reaction product is phenol but that the yield of phenol falls short of 100% of the phenyl halide hydrolyzed.

Under the conditions used a considerable amount of diphenyl ether is to be expected since Sabatier and Espil, working under conditions similar to those employed here, have shown that the system phenol–diphenyl ether–water comes to equilibrium when diphenyl ether constitutes about half, by weight, of the organic constituents.[4] Therefore, in calculating a net yield

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[4] Sabatier and Espil, Bull. *soc. chim.*, [4] 15, 228 (1914).

from the hydrolysis, phenol and diphenyl ether should be considered together. There is not enough information to permit the calculation of such a net yield from these experiments, but it should be fairly good, at least.

Experiment 4 compared with Expt. **3** indicates a decrease in activity of the catalyst due to fouling. Experiment 5 indicates that the activity of the catalyst has been restored by the burning-off process.

The first results reported in Table II show that the hydrolysis of phenyl halides may be effected by a variety of hydration catalysts. As already pointed out, the various samples of catalyst were not used in the same state of subdivision and in the same amounts. As other factors also influence the activity of contact catalysts, the results obtained for the individual samples used cannot be rigidly compared. However, it appears that silica gel and titania are the most active; kaolin is the least active; and phenol was obtained from all of the experiments except the one in which kaolin was used.

Experiments 16 to **20** were carried out to learn something of the temperature range over which the hydrolysis took place. They show that at 300° both phenyl chloride and bromide hydrolyze at a measurable speed.

Conclusions

Phenyl chloride and phenyl bromide are readily hydrolyzed to the extent of at least **25** to 40% by passage of their vapor mixed with steam over silica gel at **500** to 550° and ordinary pressures.

The ability to catalyze the hydrolysis of the phenyl halides is not peculiar to silica gel but is possessed by a variety of hydration catalysts: silica gel, titania, alumina, thoria, zirconia and the blue oxide of tungsten. A sample of kaolin showed little activity.

Silica gel and titania appear to be the most active.

With silica gel as the catalyst the reaction proceeds at a measurable speed at 300° and above.

The products of the reaction are: the halogen acid, phenol, diphenyl ether and probably smaller quantities of other organic compounds. No pronounced halogenation of the phenol obtained in the primary reaction was noticed and no water-insoluble gases were evolved.

The activity of silica gel which has been fouled by use may be restored by heating the catalyst in air or oxygen. The activity of titania can be regenerated in the same way.

NEW YORK CITY

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

STUDIES OF CONJUGATED SYSTEMS. I. THE CHLORINATION OF PHENYLBUTADIENE[1]

BY IRVING E. MUSKAT AND K. A. HUGGINS

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According to Thiele's[2] theory concerning the affinity relations in conjugated systems addition should take place in the 1,4-position. Many exceptions were found to this theory which were explained by Thiele by means of special assumptions. However, the exceptions have increased and there has arisen sharp criticism toward this theory.[3] We cannot here consider the results of the manifold investigations, indicating in each case its bearing on the Thiele theory; nor can we discuss the many explanations offered by various workers in this field regarding the mode of addition in conjugated systems. This much may be said, however, that in general there are two main views: according to the one view, held by Thiele, the addition depends merely on the valence relations in the original compound, while according to the other, the Hinrichsen view, the addition depends not only on the nature of the original unsaturated compound in which the addition is taking place, but also on the electrochemical nature of the entering atoms or groups.[4]

While not any of the many theories suggested explain all of the addition reactions to conjugated systems, nevertheless, it appears that in a series of cases the Hinrichsen view is in better accord with the facts than any of the other theories. Recent work by K. v. Auwers[5] on the addition of hydrogen and bromine to sorbinic acid and related compounds, and still more recent work by Kuhn and Winterstein[6] on the addition of hydrogen and bromine to the diphenyl-poly-enes, clearly indicate the inadequacy of the Thiele theory and offer supporting evidence for the Hinrichsen views.

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[1] Abstracted from a thesis by Mr. K. A. Huggins, presented to the Ogden Graduate School of Science of the University of Chicago in partial fulfilment of the requirements for the degree of Master of Science.

[2] Thiele, *Ann.*, 306, 87 (1899).

[3] Michael, *J. prakt. Chem.*, 60, 467 (1899); Hinrichsen, *Ann.*, 336, 174 (1904); Vorländer, *Ber.*, 36,2339 (1903); Ingold, *J. Chem. Soc.*, 121,329, 1306 (1921); Kohler, *Am. Chem. J.*, 31, 642 (1904); 33, 153, 333 (1905); 36, 529 (1907); Straus, *Ber.*, 42, 2866 (1909); Erlenmeyer, Jr., *Ann.*, **316,** 43 (1901); and many others.

[4] We shall not discuss in this paper the more recent work of Ingold, Claisen, Prevost, Farmer and others, who have shown that addition products in which the addenda are in the 1,4-positions are not necessarily due to 1,4-addition, but rather to a condition of equilibria in three-carbon prototropic systems. We shall be more concerned with the final addition product than the mechanism by which it was formed.

[5] K. v. Auwers, *Ann.*, 434, 140 (1923).

[6] Kuhn and Winterstein, *Helv. Chim. Acta*, 11, 116, 123 (1928).

Because of the theoretical importance of the addition reactions of conjugated systems it was considered desirable to make a thorough investigation of such addition processes, particularly in simple conjugated systems. The present paper contains the results of an investigation on the chlorination of phenylbutadiene.

Phenylbutadiene was prepared according to the method of Carl von der Heide[7] by the condensation of cinnamic aldehyde with methyl magnesium bromide and the subsequent hydrolysis of the intermediate Grignard addition compound with 30% sulfuric acid. In order to become familiar with the technique and procedure involved in the use of an ozonizer as a tool in the study of such reactions, it was decided to repeat Straus'[8] work on the bromination of phenylbutadiene, in which he found that only 3,4-addition occurred. We confirmed his work in every particular.[9]

The chlorination of phenylbutadiene was then studied. It was found that phenylbutadiene readily absorbs two atoms of chlorine to form a dichloride which boils at 125° under 3 mm. pressure. The chlorination was carried out in various solvents and under different experimental conditions. Chloroform, ligroin, glacial acetic acid and carbon disulfide were used as solvents and the chlorination was carried out at temperatures varying from about -80 to about 150°. The same dichloride was obtained regardless of the experimental conditions. The only effect of the temperature of chlorination was in the amount of decomposition. The dichloride is fairly unstable and loses hydrogen chloride easily, so that at higher temperatures more decomposition takes place. However, in not one of the large number of experiments performed was a different dichloride obtained.

The structure of the dichloride was determined by ozonization. Three dichlorides are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place. On ozonizing the phenylbutadiene dichloride it was possible to obtain an 83% yield of benzaldehyde as calculated from its semicarbazone and the benzoic acid that was recovered. This proves beyond any doubt that chlorine adds to phenylbutadiene in the 3,4-positions. A number of ozonizations were made but in no case was it possible to obtain even the slightest indications for the presence of any of the aldehydes or acids to be expected from the oxidation of compounds resulting from the 1,2- or 1,4-addition of chlorine.

The phenylbutadiene dichloride can be further chlorinated to give a mixture of stereoisomeric tetrachlorophenylbutanes. The tetrachloride

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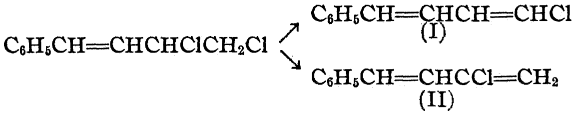
[7] Carl von der Heide, *Ber.*, 37, 2101 (1904).

[8] Straus, *ibid.*, 42, 2866 (1909).

[9] We worked up the ozonization product in a different manner. Straus obtained a 50–60% recovery of benzaldehyde, while we were able to recover 73% of the benzaldehyde.

can be completely reduced to phenylbutadiene or partially reduced with zinc to give again the same phenylbutadiene dichloride from which it was made. This shows that the chlorine is more easily removed from the 1,2-positions near the phenyl group, and again indicates the stability of the 3,4-dichloride.

Phenylbutadiene dichloride, when treated with aqueous potassium hydroxide at a temperature of 90° for several hours, loses a molecule of hydrogen chloride and is thus converted into phenylchlorobutadiene, with an almost theoretical yield. The same monochloride may be obtained by merely refluxing the phenylbutadiene dichloride for several hours, but this process entails a large loss due to polymerization. The phenylchlorobutadiene boils at 115.5° under 3.5 mm. pressure. It may be readily seen from the structure of the phenylbutadiene dichloride that hydrogen chloride may be eliminated in either of two ways, thus



$$C_6H_5CH{=}CHCHClCH_2Cl \begin{array}{l} \nearrow \; \underset{\text{(I)}}{C_6H_5CH{=}CHCH{=}CHCl} \\ \searrow \; \underset{\text{(II)}}{C_6H_5CH{=}CHCCl{=}CH_2} \end{array}$$

In order to determine the structure of the monochloride it was treated with a water suspension of silver oxide and warmed. On working up the reaction mixture y-phenylcrotonic acid ($C_6H_5CH{=}CHCH_2COOH$) was isolated. This proves conclusively that the phenylchlorobutadiene has Structure I, $C_6H_5CH{=}CHCH{=}CHCl$. Since the chlorine atom is removed from the 3-position in preference to the 4-position, it indicates that the 3-chlorine atom is relatively electronegative as compared with the 4-chlorine atom. The significance that this bears on the electronic concept of valence in organic compounds will be discussed in a later paper.

The phenylchlorobutadiene easily absorbs a molecule of chlorine to give a trichloro derivative, boiling at 140° under 5 mm. pressure. Again, there are three trichlorides that may possibly be formed, depending on whether 1,2-, 1,4- or 3,4-addition takes place. The phenylchlorobutene dichloride was ozonized in the same way as the phenylbutadiene dichloride. On hydrolysis of the ozonide formed, it was possible to recover a 50% yield of benzaldehyde as benzoic acid. The isolation of benzaldehyde proves conclusively that 3,4-addition has taken place and, therefore, the structure of the trichloride must be $C_6H_5CH{=}CHCHClCHCl_2$.

The phenylchlorobutene dichloride easily absorbs-another molecule of chlorine to give a pentachloride which boils at 162° under 5 mm. pressure. To judge from the constancy of the boiling point of the 1-phenyl-1,2,3,4,4′-pentachlorobutane, it does not consist of a mixture of stereoisomers as did the 1-phenyl-1,2,3,4-tetrachlorobutane previously described.

The experimental results recorded here lend support to the Hinrichsen view of addition to conjugated systems as contrasted to the Thiele view.

That is, the mode of addition to conjugated systems is not only a function of the conjugated compound itself, but also depends on the nature of the addendum. In general, hydrogen is added to the ends of the conjugated system, in the 1,4-positions, particularly so when the conjugation ends in oxygen $>C{=}C{-}C{=}O$. With other types of addition reagents, the halogens, halogen acids, etc., normal addition to the double bonds of the conjugated system is the rule, just as in the single ethylenic double bonds. More recent work by Ingold, Claisen, Prevost, Farmer and others seems to indicate that even in those cases where 1,4-addition is found, it is not due primarily to direct 1,4-addition but rather to a tautomerization of the 1,2-addition compounds. This will be discussed in a later paper.

Experimental Part

Phenylbutadiene Dibromide.—Phenylbutadiene was prepared according to the method of Carl von der Heide.[7] Phenylbutadiene dibromide was prepared according to the method reported by Straus.[8] The pure dibromide melted at 94°.

Phenylbutadiene dibromide (4.5 g.) was dissolved in chloroform and a current of ozonized oxygen was bubbled through the solution for several hours. An ozonizer similar to the one described by Harries[10] was used. The apparatus was arranged so that any desired ozone concentration, up to 20%, could be obtained. A 3–4% ozone concentration was used in these experiments. After the ozonization was completed the chloroform was removed by suction and the residual viscous ozonide was decomposed with water. To assure the complete decomposition of the ozonide, it was warmed on the water-bath for a short time. The mixture consisted of acids and aldehydes and was separated by extracting the alkaline solution several times with ether. The alkaline solution was then acidified and again extracted with ether. The ethereal solution was dried and the ether removed by vaporization. A solid (1.06 g.) remained which melted at 120". It was crystallized once from water and melted at 122°, the melting point of benzoic acid. A mixture with pure benzoic acid also melted at 122°.

The ethereal solution containing the aldehydes was again washed with alkali and the ether removed by vaporization. The residue, an oil, was treated with an aqueous solution of semicarbazide hydrochloride containing enough sodium acetate to neutralize the hydrochloric acid in combination with the semicarbazide. A semicarbazone (0.51 g.) was precipitated after a short time. This was removed and dried. It melted at 209°. It was recrystallized several times from alcohol and melted at 214°, the melting point of the semicarbazone of benzaldehyde. When it was mixed with the synthesized product the melting point of the mixture was not lowered. This corresponds to a 73.2% yield of benzaldehyde, while Straus was able to obtain only a 50–60% yield.

Phenylbutadiene Dichloride.—To prepare phenylbutadiene dichloride a stream of dry chlorine was allowed to pass into the pure phenylbutadiene. Absorption took place readily and the reaction mixture became very hot. Hydrogen chloride was liberated as the chlorination proceeded and the reaction mixture assumed a reddish color. When the theoretical quantity of chlorine was absorbed, the reaction mixture was distilled under reduced pressure. A light yellow oil distilled over at 125° under 3 mm. pressure. It was analyzed for chlorine by the Carius method. The analysis of the compound proves that it is a dichloride.

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[10] Houben-Weyl, "Die Methoden der Organischen Chemie," 1924, Vol. III, p. 276.

Anal. Subs., 0.2322, 0.2596: AgCl, 0.3308, 0.3698. Calcd. for $C_{10}H_{10}Cl_2$: Cl, 35.28. Found: Cl, 35.25, 35.24.

The conditions under which phenylbutadiene was chlorinated were varied considerably. Various solvents such as chloroform, ligroin, carbon disulfide and glacial acetic acid were used, and the temperature was varied from about −80° (carbon dioxide snow and ether) to about 150°. However, in all cases only one dichloride was obtained. The use of a solvent decreased the amount of tetrachlorophenylbutane obtained, and lowering the temperature decreased considerably the extent of decomposition, but no other effect was observed. The phenylbutadiene dichloride distilled over completely at constant temperature under various pressures, which eliminates the possibility that it consists of a mixture of dichlorides having a constant boiling temperature. It could not be crystallized even in carbon dioxide snow and ether; it merely solidified to a glass.

The phenylbutadiene dichloride was subjected to ozonization and the ozonide thus formed was treated in a manner entirely analogous to that of the dibromide previously described. The acid and aldehyde portions were separated, the acid portion yielding benzoic acid, which was identified by the melting point of a mixture with known benzoic acid, while the benzaldehyde was removed as the semicarbazone. which was identified in a similar manner. From 5.5 g. of phenylbutadiene dichloride it was possible to isolate 2.01 g. of benzoic acid and 1.0 g. of semicarbazone of benzaldehyde. This corresponds to an 83% yield of benzaldehyde. In some cases the ozonide was treated with hydrogen peroxide, which oxidized all of the aldehydes to their corresponding acids. From 6 g. of the dichloride it was possible to isolate 2.5 g. of benzoic acid, which was identified by the melting point of a mixture with known benzoic acid. This corresponds to a 70% yield of benzaldehyde.

This proves conclusively that chlorine had added to phenylbutadiene in the 3,4-positions and not in the 1,2- or 1,4-positions. The structure of the dichloride must be $C_6H_5CH{=}CHCHClCH_2Cl$.

Tetrachlorophenylbutane.—Phenylbutadiene dichloride was dissolved in chloroform and a stream of chlorine gas was allowed to pass in until no more was absorbed. The chloroform was removed by vaporization and the residual reddish colored oil was distilled under reduced pressure. A clear, colorless oil began to distil over at 155" under 7 mm. pressure and the temperature rose gradually, without any abrupt change, to 166°. The distillate was redistilled at 7 mm. pressure and collected in three fractions; each fraction was analyzed for chlorine by the Carius method.

Anal. Fraction I (155–160°), subs., 0.2043: AgCl, 0.4333. Found: Cl, 52.46. Fraction II (160–164°), subs., 0.2637: AgCl, 0.5567. Found: Cl, 52.22. Fraction III (164–166°), subs., 0.2950: AgCl, 0.6203. Found: Cl, 52.02. Calcd. for $C_{10}H_{10}Cl_4$: Cl, 52.18.

It is quite obvious that the tetrachlorophenylbutane consists of a mixture of possibly three stereoisomers. No effort was made to separate them. The tetrachlorophenylbutane did not crystallize even when allowed to remain in a carbon dioxide snow and ether mixture for several hours.

The Reduction of Tetrachlorophenylbutane.—If tetrachlorophenylbutane is treated with powdered zinc at room temperature no reaction takes place. However, if the reaction flask is placed on the water-bath for a short time a vigorous reaction occurs. The product of the reaction depends on the quantity of zinc used.

Tetrachlorophenylbutane was treated with slightly more than two moles of zinc and the reaction mixture was warmed on the water-bath for several hours. The reaction mixture was then extracted with ether and the ethereal solution was dried over calcium chloride. The ether was removed by vaporization and the residual oil distilled under reduced pressure. It distilled at 86° under 11 mm. pressure, the boiling point of phenylbutadiene. That it was phenylbutadiene was further confirmed by the melting point of its tetrabromide, 146°. This shows that the tetrachloride was completely reduced.

The previous experiment was repeated and slightly less than half the amount of powdered zinc was used (one mole of zinc to one mole of tetrachloride). When all of the zinc had reacted the mixture was extracted with ether, the ethereal solution dried and the ether removed by vaporization. The residual oil was distilled under reduced pressure. It distilled sharply at 125° under 5 mm. pressure, the boiling point of 3,4-dichlorophenylbutane. It was ozonized and yielded benzoic acid as one of the oxidation products. This proves conclusively that the structure of the dichloride obtained by the partial reduction of the tetrachlorophenylbutane is identical with that of the dichloride obtained on chlorinating phenylbutadiene.

Phenylchlorobutadiene.—If phenylbutadiene dichloride is treated with an aqueous solution of potassium hydroxide and allowed to stand on the water-bath for several hours, one molecule of hydrogen chloride is eliminated, forming a monochloride. The monochloride was taken up in ether, thoroughly washed free from alkali, dried over calcium chloride, filtered, and the ether removed by vaporization. The residual oil was distilled under reduced pressure. It distilled almost completely at 115.5° under 3.5 mm. pressure. When very pure it crystallized in small, colorless plates, melting sharply at 53°. It was analyzed for chlorine by the Carius method. The analysis of the compound proves that it is a monochloride.

Anal. Subs., 0.0979, 0.1774: AgCl, 0.0849, 0.1536. Calcd. for $C_{10}H_9Cl$: Cl, 21.56, Found: Cl, 21.45, 21.42.

The same phenylchlorobutadiene may be obtained by simply refluxing the phenylbutadiene dichloride for several hours. However, there is a decided difference in the yield obtained by the two methods. The first method, that of warming the dichloride with aqueous alkali, gives an almost quantitative yield of the monochloride, while the second method, refluxing the dichloride, gives about a 60% yield of the monochloride. This is due to the fact that heating promotes the polymerization of the compound.

Phenylchlorobutadiene and water were introduced into a bomb tube, the tube was sealed, placed in a bomb furnace and gradually heated to 150–170°. It was allowed to remain at that temperature for several hours. On cooling the tube was opened and the contents removed. The water solution gave a decided halogen test with silver nitrate, which showed that the chlorine had been removed by hydrolysis. The degree of hydrolysis could be readily followed by the titration of the chloride ion in an aliquot sample of the water solution. The extent of hydrolysis was never more than 3 to 4% in the several experiments that were performed. The water solution gave a positive test for aldehydes with a fuchsin solution and therefore offers supporting evidence for Structure I, $C_6H_5CH{=}CHCH{=}CHCl$. Due to the slight hydrolysis, even at higher temperatures, it was not found possible to isolate the aldehyde.

In order to increase the extent of hydrolysis of the chloride, it was treated with slightly more than two moles of silver oxide suspended in water. No reaction was evident at ordinary temperature, but when the reaction mixture was warmed on the water-bath a reaction did occur and a silver mirror was deposited on the walls of the reaction vessel. This indicates that an aldehyde was formed due to the hydrolysis of the chloride, and that the silver oxide then oxidized the aldehyde to the corresponding acid, $C_6H_5CH{=}CHCH_2COOH$. The reaction mixture was acidified with nitric acid and extracted with ether. The ethereal solution was washed several times with alkali. The alkaline washings were acidified, extracted with ether, the ethereal solution was dried over anhydrous sodium sulfate and the ether was removed by evaporation. An oil remained which was taken up in carbon disulfide. On allowing the carbon disulfide to evaporate slowly, small crystals separated from the solution. These were removed and dried; they melted at 86°, the melting point of γ-phenylcrotonic acid, $C_6H_5CH=CHCH_2COOH$. This proves that the monochloride has Structure I. $C_6H_5CH=CHCH=CHCl$.

1-Phenyl-4-chloro-Δ'-butene-3,4-dichloride.—To prepare phenylchlorobutene dichloride a stream of dry chlorine was allowed to pass into pure phenylchlorobutadiene. Absorption took place readily and the mixture became very hot. The reaction mixture assumed a dark color during the chlorination but became colorless as soon as one mole of chlorine was absorbed. It was distilled under reduced pressure, distilling over at 140" under 5 mm. pressure. It was analyzed for chlorine by the Carius method. The analysis of the compound proves that it is a trichloride.

Anal. Subs., 0.2648, 0.2196: AgCl, 0.4838, 0.4008. Calcd. for $C_{10}H_{10}Cl_3$: Cl, 45.19. Found: Cl, 45.20, 45.19.

The phenylchlorobutene dichloride was subjected to ozonization and the ozonide thus formed was treated in a manner entirely analogous to that of the dichloride previously described. The acid and aldehyde portions were separated, the acid portion yielding benzoic acid, which was identified by the melting point of a mixture with known benzoic acid, while the aldehydes were removed as semicarbazones. The semicarbazones were separated by fractional crystallization into a low-melting semicarbazone (about 130°) and a high-melting semicarbazone (about 206°). However, these could not be purified enough for identification. In another experiment the ozonide was treated with hydrogen peroxide, which oxidized all of the aldehydes to their corresponding acids. From 1.04 g. of the trichloride it was possible to isolate 0.3 g. of benzoic acid, which was identified by the melting point of a mixture with known benzoic acid. This corresponds to a 50% yield of benzaldehyde.

Pentachlorophenylbutane.—Phenylbutadiene trichloride was further treated with an excess of chlorine gas until no more absorption took place. The chlorinated product was distilled under reduced pressure. A clear, colorless oil distilled over at 162° under 5 mm. pressure. It was analyzed for chlorine by the Carius method. The analysis of the compound proves that it is a pentachloride.

Anal. Subs., 0.1941, 0.1032: AgCl, 0.4541, 0.2399. Calcd. for $C_{10}H_9Cl_5$: Cl, 57.88. Found: Cl, 57.87, 57.51.

Summary

1. By chlorination of phenylbutadiene, a dichloride is formed whose structure was proved by ozonization to be a 3,4-derivative, rather than a 1,4-derivative as required by Thiele's theory of addition to conjugated systems.

2. The 3,4-dichlorophenylbutene was further chlorinated to give tetrachlorophenylbutane. It consisted of a mixture of stereoisomers boiling from 155–166° under 7 mm. pressure.

3. Tetrachlorophenylbutane was partially reduced with zinc to give the same 3,4-dichlorophenylbutene obtained by the direct chlorination of phenylbutadiene. It was also completely reduced with zinc to give phenylbutadiene.

4. 3,4-Dichlorophenylbutene loses a molecule of hydrogen chloride to give 1-phenyl-4-chlorobutadiene. Its structure was proved by converting it to γ-phenylcrotonic acid.

5. 1-Phenyl-4-chlorobutadiene absorbed one molecule of chlorine in the 3'4-positions to give 1-phenyl-3,4,4'-trichlorobutene. Its structure was proved by ozonization.

6. 1-Phenyl-3,4,4'-trichlorobutene was further chlorinated to give 1-phenyl-1,2,3,4,4'-pentachlorobutane.

7. Straus' work on the bromination of phenylbutadiene was confirmed in every particular.

CHICAGO, ILLINOIS

[CONTRIBUTION PROM THE CHEMISTRY DEPARTMENT OP THE RICE INSTITUTE]

TETRAMETHYLENE GLYCOL AND TETRAMETHYLENE CHLOROHYDRIN

BY W. R. KIRNER AND G. HOLMES RICHTER

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Some work published by Bennett[1] suggested a new method for the synthesis of tetramethylene glycol. In the first two papers Bennett gives the preparation of b-hydroxybutyl benzyl ether and in the last paper Bennett and Hock described an experiment in which the benzyl group in an entirely different series of benzyl ethers was removed by means of hydrogen bromide, forming benzyl bromide, the residual portion of the ether remaining as an alcohol. By applying this reaction to Bennett's b-hydroxybutyl benzyl ether it was found that tetramethylene glycol could be obtained in good yield. The novelty of the reaction is the splitting of the benzyl ether with hydrogen bromide without converting either hydroxyl group of the glycol into a bromide. The glycol was characterized by preparing both the di-phenyl- and di-α-naphthylurethans.

Tetramethylene glycol has been a relatively rare substance and our purpose was to devise a method by which this valuable synthetic reagent might become more easily available. The older methods of synthesis are either very tedious or give poor yields. However, after this work had been completed an article appeared by Muller[2] describing the preparation of tetramethylene glycol by the Bouveault–Blanc reduction of diethyl succinate with a yield of 54%. This is a considerable improvement over the yield reported by Böeseken,[3] who obtained a 31% yield using the same method. Müller ascribes his higher yield to the use of thoroughly dry alcohol and a more efficient method of isolation of the final product. Miiller's method thus appears to offer the cheapest and simplest method of preparing tetramethylene glycol which has been published to date.

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[1] Bennett, J. *Chem. Soc.*, 127, 1279 (1925); Bennett and Hock, *ibid.*, 47.5, 481 (1927).

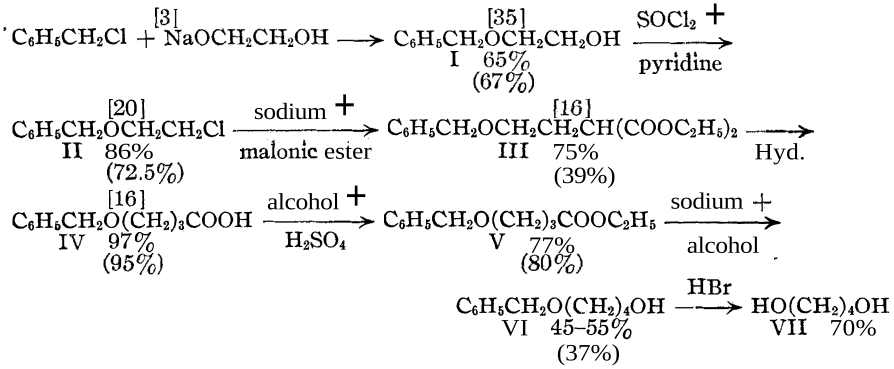
[2] Müller, Monatsh., 49, 27 (1928).

[3] Böeseken, Rec. *trav. chim.*, 34, 101 (1915).

Tetramethylene glycol was converted into tetramethylene chlorohydrin by means of Darzens' reaction,[4] with a yield of approximately 50%. Bennett and Heathcoat[5] have very recently synthesized the chlorohydrin by the action of sulfur monochloride on the glycol but they state that their method gives the chlorohydrin "in poor yield and in an impure state." They obtained a fraction boiling at 86° at 15 mm. consisting of crude tetramethylene chlorohydrin which disappeared when redistilled under reduced pressure, producing much hydrogen chloride and presumably forming tetramethylene oxide. Our product boiled at 84–85" at 16 mm. and if distilled at a pressure much higher than this it also showed a tendency to lose hydrogen chloride. However, we succeeded in obtaining a pure product (by fractional vacuum distillation), as is indicated by the good agreement obtained between the calculated and observed values for the molecular refraction and in the chlorine content. The phenylurethan and α-naphthylurethan were prepared. The former is a new compound and melted at 54°. The α-naphthylurethan melted at 69–70'; Bennett and Heathcoat give the melting point as 66°.

Experimental

The following equations illustrate the method which was used for the preparation of the tetramethylene glycol. The yield in each step is indicated under the substance prepared and Bennett's yield is given in parentheses. The figures in brackets above the various compounds indicate the number of times the quantities given by Bennett were multiplied and shows the rather large scale on which these reactions were run. The over-all yield is 11%.



$$\overset{[3]}{C_6H_5CH_2Cl} + NaOCH_2CH_2OH \longrightarrow \underset{\substack{\text{I}\ \ 65\%\\(67\%)}}{\overset{[35]}{C_6H_5CH_2OCH_2CH_2OH}} \xrightarrow[\text{pyridine}]{SOCl_2\ +}$$

$$\underset{\substack{\text{II}\ \ 86\%\\(72.5\%)}}{\overset{[20]}{C_6H_5CH_2OCH_2CH_2Cl}} \xrightarrow[\text{malonic ester}]{\text{sodium} +} \underset{\substack{\text{III}\ \ 75\%\\(39\%)}}{\overset{[16]}{C_6H_5CH_2OCH_2CH_2CH(COOC_2H_5)_2}} \xrightarrow[\text{Hyd.}]{}$$

$$\underset{\substack{\text{IV}\ \ 97\%\\(95\%)}}{\overset{[16]}{C_6H_5CH_2O(CH_2)_3COOH}} \xrightarrow[H_2SO_4]{\text{alcohol} +} \underset{\substack{\text{V}\ \ 77\%\\(80\%)}}{C_6H_5CH_2O(CH_2)_3COOC_2H_5} \xrightarrow[\text{alcohol}]{\text{sodium} +}$$

$$\underset{\substack{\text{VI}\ \ 45\text{–}55\%\\(37\%)}}{C_6H_5CH_2O(CH_2)_4OH} \xrightarrow{HBr} \underset{\text{VII}\ \ 70\%}{HO(CH_2)_4OH}$$

In the preparation of β-chloro-ethyl benzyl ether (II) by Darzens' reaction we used pyridine whereas Bennett used dimethylaniline. In our work the temperature was not allowed to rise above 55° during the addition of the thionyl chloride and the mixture was not heated to drive

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[4] Darzens, *Compt. rend.*, 152, 1314 (1911).

[5] Bennett and Heathcoat, *J.* Chem. *Soc.*, *272* (1929).

off sulfur dioxide but was merely allowed to stand overnight. This illustrates another case where good yields of a chloride can be obtained by this method without heating the reaction mixture.[6]

The improved yield of diethyl-β-benzyloxyethylmalonic ester (III) is ascribed to the use of thoroughly dried alcohol which was used in the malonic ester condensation. A good grade of absolute alcohol was further dehydrated by the irreversible hydrolysis of ethyl acetate as recommended by Smith,? and distilled directly into the apparatus used for the reaction. The mixture was merely stirred and refluxed over a period of five days and not heated under pressure as recommended by Bennett and Hock.

In the reduction of the ethyl-y-benzyloxybutyrate (V) thoroughly dry alcohol was also used. About 100 g. of ester was reduced in each run. It was found that small amounts (4–6 g.) of the glycol, which was probably formed by the splitting of the benzyl ether by the metallic sodium,[8] could be recovered from the aqueous solutions by saturating them with anhydrous potassium carbonate and then extracting with alcohol.

Bennett and Hock's procedure for the splitting of benzyl ethers was modified as follows and found to give better yields: 66 g. of the benzyl ether were treated with 175 cc. of concentrated hydrobromic acid and allowed to stand for three days (without adding any hydrogen bromide). Potassium carbonate was added until the mixture was just neutral and any unreacted material was extracted with benzene, the benzene extract being washed with water to remove any glycol. The aqueous solution, plus that obtained from washing the benzene layer, was saturated with potassium carbonate and extracted with alcohol. On distilling off the alcohol, carbonate precipitated out; this was again extracted with alcohol and the alcohol distilled off. A residue is thus obtained which is distilled in vacuum and which yields the glycol; 20.7 g. of glycol was obtained and 6.2 g. of unchanged benzyl ether was recovered. This corresponds to a yield of 69% based on the ether which reacted; boiling point of tetramethylene glycol, 107–108° at 4 mm.; melting point, 19–19.5°; $d_4^{20} = 1.0171$; n_D^{20}, 1.4467; M_D (calcd.), 23.722; M_D (found), 23.651. The di-phenylurethan was prepared according to the directions of Hamonet.[9] Crystallization from chloroform gave a product melting at 179.5". Hamonet gives the melting point as 180–181°. The di-or-naphthylurethan was also prepared by warming the glycol with or-naphthyl isocyanate. Crystallized from xylene it melted at 198.5–199°. Bennett and Heathcoat give the melting point as 198'.

Anal. Calcd. for $C_{26}H_{24}O_4N_2$: N, 6.55. Found: N, 6.49.

Tetramethylene **Chlorohydrin.**—Twenty grams of the glycol was dissolved in pyridine (17.6 g.) in a 200-cc. three-nerked flask fitted with a stirrer, dropping funnel and reflux condenser. The flask was placed in a water-bath maintained at 55° and 26.4 g. of thionyl chloride was added drop-wise during one hour. The temperature of the bath was then raised to 80° for one hour to drive off the sulfur dioxide. The reaction mixture was then worked up in the usual way; yield, 11.4 g. (47%). Tetramethylene chlorohydrin boils at 84–85' at 16 mm. If distilled at a pressure much higher than this it tends to lose hydrogen chloride, presumably forming tetrahydrofuran; d_4^{20}, 1.0883; n_D^{20}, 1.4518; M_D (calcd.), 27.064; M_D (found), 26.893.

Anal. Subs., 0.3175: AgCl, 0.4176. Calcd. for C_4H_9OCl: Cl, 32.67. Pound: Cl, 32.54.

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[6] See Kirner, THIS JOURNAL, 50, 1959 (1928).

[7] Smith, J. *Chem. Soc.*, 1288 (1927).

[8] Schorigin, *Ber.*, 56, 176 (1923); 57, 1627 (1924).

[9] Hamonet, Bull. *soc. chim.*, [3] **33,** 525 (1905).

The phenylurethan, crystallized from petroleum ether, melted at 54°. This is a new compound.

Anal. Subs., 0.0608: AgCl, 0.0381. Calcd. for $C_{11}H_{14}O_2NCl$: Cl, 15.58. Found: Cl, 15.50.

The a-naphthylurethan prepared similarly and crystallized from petroleum ether melted at 69–70'. Bennett and Heathcoat give the melting point as 66°.

Anal. Subs., 0.3401: AgCl, 0.1768. Calcd. for $C_{15}H_{16}NO_2Cl$: Cl, 12.78. Found: Cl, 12.85.

Summary

1. A new method of synthesis of tetramethylene glycol has been devised. Müller's method (published after this work had been completed), involving the reduction of diethyl succinate, appears to be cheaper, simpler and more rapid.

2. Tetramethylene chlorohydrin was isolated in a pure state for the first time; its physical properties were determined and its phenylurethan and a-naphthylurethan were made, the former being a new derivative.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF WISCONSIN, AND THE OFFICE OF CEREAL CROPS AND DISEASES, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CHEMICAL COMPOSITION OF CORN (ZEA MAYS) SEEDLINGS. I. THE ISOLATION OF XYLAN AND CELLULOSE FROM THE CELL WALLS[1,2]

BY KARL PAUL LINK

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Introduction

In the course of a general investigation on the nature of corn (Zea Mays) seedling blight, it was deemed expedient to investigate the chemical com-

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[1] Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

[2] This publication comprises part of a thesis submitted to the Graduate Faculty of the University of Wisconsin in June, 1925, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The research was concluded during 1925–1927 while the author was a Fellow of the International Education Board posted at the University of St. Andrews, Scotland, and the University of Graz, Austria. The author wishes to acknowledge his indebtedness to Sir James Irvine, D.Sc., F.R.S., Principal and Vice Chancellor of the University of St. Andrews, for the privilege of extending the research while a student in his laboratory and for advice and help received. The author is likewise indebted to Professor Fritz Pregl, Director of the Medico-chemical Institute of the University of Graz, under whose personal direction the micro-analytical analyses were conducted. To the Board of Directors of the International Education Board, New York City, the author wishes to extend his thanks for the Fellowship grant received which enabled him to complete the work in the laboratories mentioned.

position of the seedlings with the purpose of correlating chemical composition with disease resistance. A preliminary report was made in 1923,[3] wherein the general purposes of the investigation were presented. This paper deals primarily with the studies made to determine the nature of the chemical constituents that compose the cell walls of the corn seedling.

It is of importance, and also of general interest to plant biochemistry, to know whether the environmental factor, temperature, can modify or alter the nature of the chemical components laid down in the cell wall. Of equal significance is the question, "Are the cell wall substances formed in the early stages of plant growth the same as those in the mature plant?" In cellulose chemistry the question frequently arises,[4] "Is there one true cellulose, $(C_6H_{10}O_5)_n$, universally distributed throughout nature, and made up of glucose units linked in an identical manner, or are there many types and kinds of cellulose?" The criterion commonly used to designate a true cellulose is the cotton fiber. Cotton is regarded as the standard example of a normal cellulose.[5]

The corn seedling lends itself very readily to a study of the general considerations mentioned. Very sensitive responses to the environmental factor of temperature are exhibited by the corn plant. At the optimum growing temperature, 24°, the rate of development of the seedlings is approximately four to five times that attained at the temperature of 12". The cell walls of the corn seedling are relatively free from lignin. In the epidermal and endospermal layers there are some suberized and cutinized cells, but the incrustating substances are of such a nature that they can be readily removed. The necessity of applying strong oxidizing reagents to approach the study of the polysaccharide constituents is thereby eliminated. Nitrogenous substances of a very stable and resistant nature are likewise not found in the corn seedling. The nitrogenous compounds present can be readily removed without attacking the basic cell wall structure.

Experimentation

The studies here recorded were conducted on two lots of corn seedlings produced at 12 and 24°.[6] The separate batches of seedlings were grown in soil in the Wisconsin

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[3] Dickson, Eckerson and Link, Proc. *Nat.* **Acad.** *Sci.,* **9, 343 (1923).**

[4] Irvine and Hirst, J. *Chem. Soc.,* **125,** 15 **(1924);** Heuser, "Lehrbuch der Zellulosechemie," Gebrüder Borntraeger, Berlin, 1927, 3d ed.

[5] Hess, "Die Chemie der Zellulose und ihrer Begleiter," Akademische Verlagsgesellschaft, Leipzig, 1928. This work also contains a very complete treatise on the chemical nature of the substances that accompany cellulose in nature.

[6] The results presented throughout the experimental part of this paper are those obtained by the study of seedling tissue grown at 24°. Tissue grown at 12° was studied in the same manner. The general analytical results obtained from comparable preparations of either 12 or 24° tissue were the same. The quantitative differences found are referred to in the discussion and will be presented in detail in a forthcoming publication.

constant temperature chambers[7] to the same stage of development. The seedlings planted at a depth of two and one-half inches were harvested when they reached the stage where the coleoptile ruptured the leaf sheath. At 24° five days are required, while at 12° the seedlings reach this stage in twenty to twenty-two days. After removing the soil by washing with water, the sprouts (radicle and plumule) were separated from the endosperm and immediately steeped in 95% alcohol.[8] A sufficient quantity of alcohol was used to keep the final concentration above 70% after dilution by the water from the tissue. The alcohol was subsequently boiled under a reflux condenser for five hours to kill the tissue.

Preliminary Extraction to Remove Non-polysaccharide Substances.—The alcohol in which the seedlings were preserved was filtered off at the pump. The tissue was then ground in a Nixtamal mill using alcohol as the liquid medium. It was subsequently transferred to a large Soxhlet, after Sando,[9] and extracted, first with 90% alcohol for twenty-four hours and finally with 99% alcohol for ten hours. After the alcohol imbibed by the tissue had been removed in a current of air at 25°, the tissue was ground in a drug mill and finally in a ball mill until all particles could pass through a 120-mesh sieve. It was then extracted for twenty-four hours with ether in a Soxhlet and finally with petroleum ether (b. p. 90–110°). The use of the fat solvents was found to be very advantageous since they removed wax and gum-like substances that had remained intact during the alcohol extraction.

Extraction of Protein, Pectin and Incrustating Substances.—After the removal of the fats, pigments and sugars, the tissue was digested for thirty-six hours in 1% ammonium hydroxide solution at 25°, and pressed free from the extraction liquors in a hand press. The excess ammonia was removed by washing with warm water (65°).

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[7] Jones, Johnson and Dickson, Wisconsin Agr. Exp. Sta., Bull., 71 (1926).

[8] In all of the investigations conducted on the nature of the cell wall constituents of the corn seedling, it was found advantageous to refrain from dehydrating the green seedling tissue by the direct application of heat. The seedlings were therefore killed by steeping them in alcohol. They were also preserved in this medium. The various fractions extracted from the cell walls were likewise never dehydrated above the temperature of 25" until most of the moisture (96–98%) had been removed through the use of organic solvents. Alcohol of successively increasing concentrations and then dry ether were used to dehydrate the preparations. By the application of these solvents a flaky and friable physical consistency was always secured in all of the products obtained. The products were also always remarkably free from discoloration.

If a freshly precipitated xylan preparation is dehydrated directly, either by the application of a current of air or in a vacuum desiccator over calcium chloride, a hard, cohesive, leathery, discolored mass is obtained, from which the last traces of water cannot be removed except by heating in a vacuum at 95° for an extended period. A xylan product prepared by direct dehydration has quite different solubility properties than one first dehydrated by the use of organic solvents. Thus a xylan preparation dehydrated directly over calcium chloride was found to be only partially soluble in hot water and required fourteen hours for complete solution in 1% sodium hydroxide, whereas a similar preparation first dehydrated in alcohol and ether and then over calcium chloride, was readily soluble in boiling water and went into solution in 1% alkali in one hour at 22°. A cellulose preparation dehydrated at 30° in a current of air could not be converted into the triacetate by the method used in this investigation. It was likewise only slowly soluble in Schweitzer's reagent. On the other hand, the cellulose preparations that had first been dehydrated by the use of organic solvents could be readily acetylated and dissolved rapidly in Schweitzer's reagent.

[9] Sando, *Ind. Eng. Chem.*, 16, 1125 (1924).

This extraction was then followed by the chlorine dioxide–sodium sulfite treatment of Schmidt and Graumann,[10] to remove coloring matter and residual lignin- and cutin-like substances. After six treatments with an aqueous chlorine dioxide solution containing approximately 0.25% of the gas, followed successively by six treatments with 2.0% sodium sulfite, these reagents had no further effect. By washing copiously with water at 65° the free chlorine and sodium sulfite were removed from the tissue. The water imbibed by the remaining polysaccharide substances was removed by suspending the residue for twelve hours, first in 95%, then in 98%, and finally in 99.5% alcohol, after which the alcohol was removed by shaking in a large quantity of absolute ether for fifteen hours. By drying in a vacuum desiccator (15-mm. pressure at 25°) over calcium chloride, the ether and any traces of alcohol still remaining were removed. From the aforementioned extractions the final product obtained was a snow-white amorphous powder.

Extraction of **Xylans.**[11]—One hundred grams of the dry product prepared as above, containing 0.33% of ash and 0.67% of nitrogen, was successively extracted five times for twenty-four hours with one liter of 5.0% sodium hydroxide (carbonate free) by shaking on a machine in a glass-stoppered bottle containing small glass rods. A sixth extraction did not remove more material. To the combined alkaline extracts 95% alcohol was added until complete precipitation was produced. The xylan precipitate was allowed to settle, whereupon the major portion of the liquid could be siphoned off. It was found that the precipitated xylan was most efficiently washed free from alkali. by centrifuging, using 50% alcohol containing 10% acetic acid as the washing medium. It was then suspended in 95% alcohol for twelve hours and finally in 99.5% alcohol for twenty-four hours. The alcohol in turn was replaced by ether. Approximately 23.0 g. of xylan was obtained. This is equivalent to 8.5-9.0% of Xylan A, based on the original dry weight of the seedlings. The analysis and properties of this preparation designated as Xylan A are given below.

Extraction of Xylan **B.**—The cell wall material, intact after the separation of Xylan A, had an ash content of 0.37% and contained 0.36% of nitrogen. The quantity of xylan determined by the 12% hydrochloric acid distillation after Krober and Tollens[12] was 11.0% (based on the dry weight of the Xylan A free residue). The residue freed from Xylan A was therefore subjected to a 10% sodium hydroxide (carbonate free) extraction at 60° in the identical manner described above. After four extractions no more xylan was removed. The xylan was precipitated, washed and dried as already described. The yield of Xylan B was approximately 3.0–4.0%, based on the original dry weight of the seedling tissue.

Purification of Xylan **A.—Xylan** A was purified by reprecipitating it from an ammoniacal copper hydroxide solution after a method similar to that employed by Hess.[13] Ten grams was dissolved in 1 liter of 25.0% ammonium hydroxide containing 10 g. of copper hydroxide. By shaking the solution for one hour practically complete solution was obtained. A small amount of flocculent matter remained which was

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[10] Schmidt and Graumann, *Ber.*, **54**, 1860 (1921).

[11] The term hemicellulose was employed by C. Schulze, *Z. physiol. Chem.*, 16, 387 (1892), to denote a substance similar in character to cellulose, which is easily hydrolyzed by weak acids. The Xylans A and B, extractable with 5 and 10% alkali, are likewise quantitatively removed by a 2.50% sulfuric acid hydrolysis. They are therefore hemicelluloses according to the Schulze classification. The writer prefers the more exact terminology, Xylan A and B, to the term "Hemicellulose."

[12] Kröber and Tollens, *J. Landwirtsch.*, **48**, 357 (1900); *Z. angew. Chem.*, **15**, **477** (1902).

[13] Hess, Messmer and Ljubitsch, *Ann.*, **444**, 287 (1925).

removed by centrifuging. This material had a nitrogen content of 8.0%. It was therefore not further considered since it was undoubtedly of a proteinaceous nature. To the clear solution obtained after the removal of the afore-mentioned nitrogen-containing substance, glacial acetic acid was added until the solution was just faintly alkaline. The xylan was thereby precipitated, centrifuged and washed, first with 50% alcohol containing 10.0% of acetic acid to remove the copper, and finally with 95.0% ethyl alcohol to remove the acetic acid. The water was removed with alcohol and the alcohol with ether as stated above.

Properties of Xylan A.—The xylan product obtained consisted of a fine, snow-white amorphous powder, free from nitrogen[14] and contained only 0.22% ash. It is soluble in hot water and forms a thin jell on cooling which exhibits marked swelling properties when alcohol is added. In weak alkalies it is readily soluble at room temperature and can be quantitatively thrown out of solution by the addition either of acidified alcohol or glacial acetic acid. It does not reduce Fehling's solution and is levorotatory. The specific rotation (2-dcm. tube) in 1% sodium hydroxide lies between the values —80.00 and —83.86' (the specific rotation of the various xylans so far isolated varies between the values —70 to —85°).[15] The ultimate analysis showed C, 45.23; H, 6.09 (Pregl-micro method). Calcd. for xylan, $(C_5H_8O_4)_n$, 132.06: C, 45.44; H, 6.11. Distillation with 12% aqueous hydrochloric acid gave an amount of furfural estimated as the phloroglucide compound corresponding to 94.6% of xylan. In view of the later experiments reported, which indicate the absence of other pentoses, the figures quoted refer to pentosans in the form of xylan.

Hydrolysis of Xylan A.—Two grams of Xylan A corrected for ash and moisture were treated with 10 cc. of 72.0% sulfuric acid at 15° for two hours. Within this time solution was invariably complete. After adding sufficient water to produce a 2.0% acid solution, the solution was heated under a reflux condenser for two hours. In some of the preparations a very small amount of flocculent material resisted hydrolysis. After cooling, the solution was neutralized with the requisite quantity of barium carbonate and filtered at the pump. The barium precipitate was extracted twice with boiling water, the washings were combined with the original filtrate and concentrated to a sirup in a vacuum of 15 mm. at 45°. The sirup was taken up with water, filtered free from a small inorganic residue, clarified with activated blood charcoal, again filtered and finally made up to a volume of 100 cc. The reducing value of 10-cc. aliquots was determined by the Shaffer and Hartmann[16] method: found, 93.30%, calculated as xylose. Arabinose was absent from the hydrolyzed solution, since the di-phenylhydrazine test of Neuberg[17] was negative. The phenylosazone of xylose, m. p. 154–159 (from alcohol),

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[14] The preparations are designated nitrogen-free on the basis of the macro-Kjeldahl method. Ridge, *Textile Institut*, **15**, 94 (1924); *C. A.*, **18**, 1752 (1924), has shown that when the nitrogen content of supposedly nitrogen-free cotton fibers (fibers subjected to the bleaching and weak alkali washing process) is determined by a method capable of detecting a nitrogen content of the low order of 0.001%, the fibers still contain approximately 0.035% of nitrogen. Nitrogen determinations made by the Pregl-micro Kjeldahl method on the various xylan and cellulose preparations reported in this paper never revealed a significant nitrogen content. The highest nitrogen value found was in a cellulose prepared from seedlings grown at 12° wherein the nitrogen content was 0.053% (Pregl-micro Kjeldahl method). It is therefore reasonable to regard the preparations as practically nitrogen free.

[15] B. Tollens, "Kurzes Lehrbuch der Kohlenhydrate," Barth, Leipzig, **1914**, 3rd ed., p. 475.

[16] Shaffer and Hartmann, *J. Biol. Chem.*, *45*, 365 (1921).

[17] Neuberg and Wohlgemuth, *Z. physiol. Chem.*, *35*, 40 (1902).

was obtained by treating a portion of the hydrolyzed solution with phenylhydrazine and sodium acetate. No mannose phenylhydrazone separated. The crude osazone precipitate obtained was completely soluble in dry acetone, which indicates that the osazone of glucose was not present. As a means of further identification, the Bertrand test for xylose was applied.[18] The characteristic boat-shaped needles of the double cadmium salt, $(C_5H_9O_6)Cd_2 + CdBr_2 + 2H_2O$, were obtained. The xylose was also procured in the free state by taking up the sirup from the hydrolysis of 5 g. of the xylan in enough absolute alcohol to insure complete solution. The alcohol was then concentrated until turbidity set in, whereupon glacial acetic acid was added. On seeding with an authentic specimen of d-xylose and standing for forty-eight hours in an ice chamber, the xylose crystallized out; yield, 3.96 g., 70.0% of the theoretical; m. p. 140–143°, $[\alpha]^{20}_{D}$ in water, +18.1°.

The above critical examination of the fraction extracted with 5% sodium hydroxide, designated as Xylan A, shows conclusively that it is an authentic xylan, uncontaminated with either arabinose, mannose or glucose.

Purification, Properties and Analysis of Xylan B.—Xylan B was purified and analyzed in the identical manner prescribed for Xylan A. The general properties were much the same. Xylan B was found to be free from arabinose, mannose and glucose. The ultimate analysis was in agreement with the theoretical value for $(C_5H_8O_4)_n$, the furfural yield was 93.5% and the percentage of xylose determined by reduction after the acid hydrolysis was 91.2%. The furfural and reducing value are slightly lower than those reported for Xylan A. The specific rotation in 1% sodium hydroxide was —79.20". The amount of flocculent material that resisted the sulfuric acid hydrolysis was appreciably more than that of Xylan A. This undoubtedly accounts for the lower furfural and reducing values as well as the lower specific rotation.

Isolation of Pure Cellulose, $(C_6H_{10}O_5)_n$.—The cellular residue still intact after the 10% sodium hydroxide extraction was washed free from alkali, first with 50% alcohol containing 10% acetic acid and subsequently with 65% alcohol. It was then dried in alcohol and ether. The product was free from nitrogen and contained 0.69% of ash, mostly silicon dioxide. Although no more pentose-yielding extracts could be obtained with alkali, the product still gave considerable furfural when subjected to the 12% hydrochloric acid Kröber–Tollens distillation. The yield of furfural varied between 2.3 and 4.6%. The residue also liberated carbon dioxide when heated with 12% hydrochloric acid after the method of Nanji, Paton and Ling.[19] The furfural-yielding substances present, *which are not true pentosans,* belong either to the class of cellulosic compounds that Hägglund[20] terms furfuroids or are similar to oxidized celluloses. Heuser and Stöckigt[21] reported that the so-called oxidized cellulose liberates carbon dioxide when heated with dilute hydrochloric acid. The possibility that the carbon dioxide and furfural might come from glucuronic acid residues as Schmidt and coworkers[22] have found must also be considered.

To remove these ill-defined and poorly characterized substances it was necessary to subject the residue remaining after the Xylan B extraction to two two-hour treatments at 30° with 15% sodium hydroxide. The characterization of the substances extracted with the 15% alkali is now in progress. Due to the present lack of concise information on this class of substances, a detailed discussion will be deferred. The residue remaining after the 15% sodium hydroxide extraction was washed free

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[18] Bertrand, *Bull. soc. chim.,* [3]5, 556 (1891).

[19] Nanji, Paton and Ling, *J. Soc. Chem. Ind.,* 44, 253T (1925).

[20] Hägglund, "Holzchemie," Akademische Verlagsgesellschaft, Leipzig, 1928, p. 73.

[21] Heuser and Stöckigt, *Celluloschemie,* 3, 61 (1922).

[22] E. Schmidt, K. Meinel and E. Zintl, *Ber.,* 60, 503 (1927).

from alkali and dried in the manner previously described. Fifty grams of a xylan-free residue yielded approximately **40.0** g. of a white, amorphous product. The cellulose prepared from corn seedlings, which had first been extracted with alkali until all xylan, furfuroid and oxidized cellulosic material had been removed, displays the important chemical properties of cotton cellulose.

Analysis of the Cellulose.—The ash content was **0.86%** (silicon dioxide). It was free from nitrogen. The ultimate analysis showed C, **44.40;** H, **6.15.** Calcd. for $(C_6H_{10}O_5)_n$: C, 44.44; H, **6.21.** With the zinc chloriodide reagent the cellulose preparation gives the characteristic violet color. It is completely soluble in ammoniacal copper solutions (Schweitzer's reagent) and can be quantitatively reprecipitated by the addition of acetic acid.[23] When subjected to the **12%** aqueous hydrochloric acid distillation of Krober and Tollens the cellulose yielded only traces of furfural. Only minute quantities of carbon dioxide are formed in the same distillation determined by the method of Nanji, Paton and Ling.

The triacetate, $(C_6H_7O_5(CH_3CO)_3)_n$, was prepared after the excellent method of Barnett, as modified by Irvine and Hirst[24] for the preparation of esparto cellulose triacetate. It was snow-white in color and differed from cotton cellulose acetate prepared in the same manner by being more flaky and softer in texture. The specific rotation of a chloroform solution (c = **1.3)** was **−22.1°**; moisture content, **1.08%;** ash, **0.28%;** **C, 49.85;** H, **5.35** (Pregl-micro method). Calcd. for C, **50.00;** H, **5.55.** The acetyl value calculated as acetic acid was **62.2%.** The theoretical value for cellulose triacetate is **62.51%.**

The yield of α-cellobiose-octa-acetate, $C_{12}H_{14}(COCH_3)_8O_{11}$, obtained by subjecting the cellulose to a simultaneous acetylation and hydrolysis varies between the values of **46** and 48% after the method of Hess[26] and **38** to **40%** after the method of Freudenberg.[26] After purification according to the method used by Hudson,[27] the octa-acetate showed m. p. **223°** and specific rotation in chloroform +41.6°. The accepted values are m. p. 221.5–222°, $[\alpha]^{20}_{D}$ in chloroform +41.3°. The yield of glucose, obtained as the methylglucoside, $C_6H_{14}O_6$, using the method of Irvine and Hirst, was 90.0% of the theoretical. The methylglucoside showed a permanent specific rotation of +157.2° in water and the m. p. 165–166°. Its methoxyl content was **7.68%** (Pregl-micro Zeisel method); theoretical: OCH_3, **7.77.** The only osazone detectable after hydrolysis with sulfuric acid, as described under Xylan A, was the osazone of d-glucose m. p. **204–208°.** Xylose, mannose and galactose (by mucic acid method) were absent.

Discussion

The cell walls of the corn seedling contain xylan, $(C_5H_8O_4)_n$. The total xylan content as determined by the furfural distillation and estimated as the phloroglucide compound varies between 10–12% of the original dry weight of the tissue. The xylan can be fractionated. Approximately 85–90% of the xylan is extractable with 5% sodium hydroxide (Xylan A), the remainder can be extracted with 10% sodium hydroxide (Xylan B).

In their purified state the two xylans, A and B, are snow-white amor-

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[23] The specific rotation values of the corn seedling cellulose in alkaline copper solutions determined after the method of Hess, *Ann.*, 466, 1 (1928), will appear in a subsequent publication.

[24] Irvine and Hirst, *J. Chem. Soc.*, 121, **1585 (1922);** 125, **15 (1924).**

[25] Hess, **Ann.**, 296, **309 (1925).**

[26] Freudenberg, Ber., 54, 767 **(1921).**

[27] Hudson and Johnson, THIS JOURNAL, 37, **1276 (1915).**

phous powders, soluble in boiling water and readily soluble in 1% sodium hydroxide. The chemical analysis and a study of their properties showed them to be essentially identical. They differ from each other in their initial solubility and in their behavior toward the zinc chloriodide reagent. This color test was until recently regarded to be specific for true cellulose.[28] One of Hess' co-workers[29] was the first to show that it was not specific for cellulose. Lüdtke found that a mannan isolated from the ivory nut gave a positive test with the reagent. Hess and Lüdtke[30] have also reported that a xylan from bamboo stalks gives a positive test, whereas a xylan isolated from the sulfite liquors of pine wood did not give the test. The Xylan A isolated from the corn seedling gave no color with the reagent, whereas Xylan B gave the typical violet color, formerly prescribed as specific for cellulose. A satisfactory explanation for this difference in apparently similar xylans is wanting. The ultimate composition agreed with the calculated value for $(C_5H_8O_4)_n$. The specific rotation determined in 1% sodium hydroxide varied between the values —79.20 to —83.00'. In each case the osazones obtained after hydrolysis with acid were identical under the microscope and melted at 154–160° without decomposition. The recrystallized xylose showed the correct initial and permanent specific rotation of $[\alpha]_D^{20} + 18.0$ and melted at 140–143°.

Although the xylans prepared from corn seedlings grown at 12 and 24°, respectively, are identical chemically, there is a quantitative difference in the distribution of the xylan fractions. The seedlings grown at 12° contain 10–15% more Xylan A than the 24° seedlings. Xylan B varies proportionally, being lower in the 12° seedlings than in the 24° seedlings. The total xylan content of the seedlings is approximately the same at either temperature. Chemically the xylan of the corn seedling is identical with the xylan of the mature corn plant (forthcoming paper). Its properties are similar to those assigned by other workers to xylans from various sources.[31]

About 7% of the furfural-yielding substances in the corn seedling are not true pentosans. These substances appear to be similar to the poorly characterized oxidized celluloses and furfuroids (see Hagglund, "Holzchemie" and Hess, "Chemie der Zellulose." They can be brought into solution by the use of 15% sodium hydroxide. In a forthcoming paper these substances will be discussed.

It has also been shown that the cell wall of the corn seedling contains pure

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[28] C. van Wisselingh, "Die Zellmembran," Gebrüder Borntraeger, Berlin, 1926, p. 45.

[29] Lüdtke, *Ann.*, 456, 201 (1927).

[30] Hess and Lüdtke, *ibid.*, 466, 23 (1928).

[31] Wheeler and Tollens, *ibid.*, 254, 304 (1889); Tollens, *Ber.*, 23, 2990 (1890); Thornsen, *J. prakt. Chem.*, 19, 146 (1879); *Ber.*, 13, 2168 (1880); 40, 136 (1881); Hess and Ludtke, *Ann.*, 466, 18 (1928); 466, 27 (1928); O'Dwyer, *Biochem. J.*, 17, 501 (1923).

cellulose. Approximately 14–18% of the dry weight of corn seedlings is composed of authentic cellulose possessing the formula $(C_6H_{10}O_5)_n$ and convertible quantitatively into glucose on hydrolysis. The cellulose in corn seedlings, when freed from xylan and furfuroids by alkali, displays the essential chemical properties of cotton cellulose. The ultimate analysis agreed with the theoretical value of $(C_6H_{10}O_5)_n$; it is soluble in Schweitzers reagent and can be quantitatively reprecipitated. The triacetate was identical with cotton cellulose triacetate prepared in the same manner (see Table I). Hess ("Chemie der Zellulose," p. 391) has shown that cellulose acetate preparations obtained by various methods can be regarded as chemically identical even though they show some variance with respect to the physical properties like solubility, swelling properties, viscosity in solution, and film-building capacity. The variations are presumably due to the phenomenon of molecular association so commonly exhibited by solutions of polysaccharide substances. The corn seedling cellulose can also be converted into cellobiose-octa-acetate in yields comparable to those obtained with cotton cellulose. Corn seedlings produced at 24° contain approximately 4% more true cellulose than the 12" seedlings, but the cellulose in both cases is identical.

Physiologically it is significant that cell walls of four-day-old corn seedlings grown at 24° and twenty-day old seedlings grown at 12° (same stage of anatomical development) contain the same xylan, $(C_5H_8O_4)_n$, and the same cellulose, $(C_6H_{10}O_5)_n$, found in mature corn plants and in mature plants of other species. In the cell walls of the corn seedlings the basic structural cellulose has intimately associated with it the pentosan xylan. Xylose usually accompanies glucose in nature since these two sugars are structurally related. How the xylan is actually associated with the cellulose is unknown.

The researches of Irvine and Hirst[4] have illustrated the intimate association of xylan and cellulose in esparto grass. Hess and Lüdtke[30] have reported the simultaneous occurrence of xylan and cellulose in pine wood. Lüdtke[32] has found the same to be true in bamboo stalks. Hägglund and co-workers'' have likewise recorded the accompaniment of xylan with cellulose in pine wood.

Through the brilliant contributions of Haworth,[34] Hirst,[35] Levene,[36] and others we now know that in their stable forms d-glucose and d-xylose have the 1,5-oxide ring structure. From Haworth's work[37] it is easy to perceive

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[32] Lüdtke, *Ann.*, 466, 27 (1928).

[33] Hägglund, Klingstedt, Rosengrist and Urban, *Z. physiol. Chem.*, 177,248 (1928).

[34] Haworth, Charlton and Peat, J. *Chem. Soc.*, 127, 85 (1926).

[35] Hirst, *ibid.*, 127, 350 (1926).

[36] Levene and Meyer, J. *Biol. Chem.*, 60, 167 (1924); Levene and Simms, *ibid.*, 68, 737 (1926).

[37] Haworth, J. *Soc. Chem, Ind.*, 28, 295T (1927); *Helv. Chim. Acta*, *11*, *534* (1928).

how d-glucose through oxidation and subsequent decarboxylation of the resulting uronic acid could give rise to d-xylose.

Lüdtke has demonstrated that the cellulose in the ivory nut[29] and in bamboo stalks[32] is a true cellulose. To this list can be appended the cellulose of the corn plant. It appears that there is one true cellulose, $(C_6H_{10}O_5)_n$, universally distributed in the plant world.

TABLE I

COMPARISON OF THE PROPERTIES OF CELLULOSE TRIACETATE PREPARED FROM CORN SEEDLINGS WITH COTTON CELLULOSE TRIACETATE PREPARED BY VARIOUS METHODS

Cellulose and method of preparation	% AcOH, calcd. 62.51%	Spec. rot. in $CHCl_3$	M.w. in glac. AcOH	Visc. of 20% $CHCl_3$ soln.	Film properties
Cotton cell. acet. in benz.[a]	62.51	−22.06	280	Viscous	High elast.
Same acet. in pres. of $ZnCl_2$[a]	62.61	−22.62	272	Viscous	High elast.
Same acet. with CH_3COBr[a]	62.22	−19.50	280	Sl. visc.	Low elast.
Same acet. by Barnett meth.	62.60	−21.50	Not. det.	Viscous	High elast.
Corn cell. by Barnett meth.	62.60	−22.10	Not. det.	Sl. visc.	Low elast. and brittle

[a] Cited from Hess, "Die Chemie der Zellulose," p. 392.

The author wishes to acknowledge his indebtedness to Dr. James G. Dickson, Department of Plant Pathology, and Prof. W. E. Tottingham, Department of Agricultural Chemistry, for advice and criticism received throughout the course of the investigation.

Summary

1. Corn seedlings grown at 12 and 24° to the stage where the coleoptile ruptures the leaf sheath contain 10–12% of xylan, $(C_5H_8O_4)_n$, and 16–18% of $(C_6H_{10}O_5)_n$ cellulose.
2. The xylan can be fractionated, 85–90% can be extracted with 5% sodium hydroxide (Xylan A) and the remainder with 10% sodium hydroxide (Xylan B).
3. In the pure state the Xylans A and B are soluble in hot water, are strongly levorotatory and can be quantitatively hydrolyzed into d-xylose.
4. The hexose cellulose is composed entirely of glucose residues, is convertible into cellulose triacetate, into cellobiose-octa-acetate and into the methyl glucoside. In these respects and also in its high molecular complexity the compound resembles the cellulose of cotton.
5. No sugars other than xylose and glucose have been detected in the hydrolysis products obtained from the cell wall constituents of the corn seedling.
6. Temperature does not alter the qualitative nature of the xylan and cellulosic constituents laid down in the cell walls, but alters slightly their quantitative distribution.
7. The xylan of the corn seedling is similar to the xylans obtained from

other plant species. The cellulose is identical with the normal cotton cellulose.

DEPARTMENT OF AGRICULTURAL CHEMISTRY
MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF WISCONSIN, AND THE OFFICE OF CEREAL CROPS AND DISEASES, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CHEMICAL COMPOSITION OF CORN (ZEA MAYS) SEEDLINGS. II. THE ISOLATION OF A DEXTRIN SIMILAR TO THE TRIHEXOSAN OBTAINED BY THE THERMAL DEPOLYMERIZATION OF POTATO STARCH

BY KARL PAUL LINK[1]

RECEIVED MARCH 23, 1929 PUBLISHED AUGUST 7, 1929

Introduction

Dextrins are usually regarded as the intermediate products formed in the course of the hydrolysis of starch to maltose and glucose by diastatic enzymes.[2] Numerous dextrins formed in the course of the degradation of the starch molecule have been studied by various early workers;[3] recently more thoroughly by Samec[4] and Ling and Nanji.[5]

The occurrence of dextrins or dextrin-like substances in the growing plant has frequently been reported.[6] In no case, however, have the dextrins been isolated in a sufficiently pure state to permit definite characterization

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[1] This publication comprises part of a thesis submitted to the Graduate Faculty of the University of Wisconsin, in June, 1925, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The research was concluded during 1925–1927 while the author was a Fellow of the International Education Board posted at the University of Zurich, Switzerland, and the University of Graz, Austria. The author wishes to acknowledge his indebtedness to Prof. Paul Karrer, Director of the Institute of Chemistry, University of Zurich, for the privilege of extending the research while a student in his laboratory and for advice and help received. The author is likewise indebted to Professor Fritz Pregl, Director of the Medico-Chemical Institute of the University of Graz, under whose personal direction the micro-analytical analyses were conducted. To the Board of Directors of the International Education Board (New York City) the author extends his thanks for the Fellowship grant which enabled him to complete the work in the laboratories mentioned.

[2] (a) H. Pringsheim, "Die Polysaccharide," Springer, Berlin, **1923**, 2d ed., p. 155; (b) C. Brown, "Handbook of Sugar Analysis," John Wiley and Sons, Inc , New York, **1912**, pp. 685–690.

[3] Ref. 2 b, p. 685.

[4] Samec, *Kolloid-Chemie Beikefte,* **10**, 289 (1919).

[5] Ling and Nanji, *J. Chem. Soc.,* **123**, 2666 (1923); **127**, 629 (1925); **127**, 637 (1925).

[6] (a) F. Czapek, "Biochemie der Pflanzen," Fischer, Jena, **1922**, 3d ed., Vol. I, p. 441; (b) C. Wehmer, "Die Pflanzenstoffe," Fischer, Jena, **1911**, numerous citations.

and identification. The order of the molecular aggregation of the dextrins present in plant tissue may vary from $(C_6H_{10}O_5)_2$, the anhydride of maltose, to the high state of polymerization found in starch, $(C_6H_{10}O_5)_n$. It is also possible that many of the dextrins reported present in the growing plant belong to the cellulose dextrin series and represent intermediate compounds used in the formation of cell wall tissue.

In 1922 Pictet[7] reported the isolation of a trihexosan, $(C_6H_{10}O_5)_3$, obtained by the thermal depolymerization of potato starch in glycerin at the temperature of 200–210°. By heating potato starch in glycerin until the solution just failed to give a color reaction with iodine, and then quickly removing the solvent by vacuum distillation at the same temperature, a transparent, vitreous, light brown solid was obtained, soluble in water and precipitable with ethyl alcohol. Upon purification by reprecipitating with alcohol, the product was procured as a white, amorphous, slightly hygroscopic powder, molecular weight, 503; α_D^{20} + 162.2 in water. Sjöberg[8] reported the formation of a dextrin, by the action of amylose on amylopectin, identical with the trihexosan of Pictet. The same product was obtained by Pringsheim by the action of glycerin on glycogen at the temperature of 200°.

Since 1922 it has been known[10] that the radicle and plumule of corn seedlings (Zea Mays) contain dextrins, varying in amounts from 1.25 to 3.00% of the total dry weight of the seedlings. The dextrin content was found to be highest in seedlings grown near the optimum temperature of growth, namely, at 24–28°. At these temperatures the quantity of dextrin present is usually double the value found in seedlings grown at 12–14°.

It was noted that the dextrins present in the seedlings grown at 24–28° could be roughly divided into two fractions. The fractions were both soluble in water and dilute alcohol (below 40%) but insoluble in alcohol of over 80% concentration. By adding sufficient alcohol to an aqueous solution of the dextrins to insure a concentration of 40%, one fraction was precipitated which gave a faint red color with iodine solution. By increasing the concentration of the alcohol to over 75%, a second fraction fell out, which in the crude state gave a faint yellow test with iodine. Enough of this second fraction was prepared to enable a study to be made thereupon. The dextrin fraction precipitated by 75% alcohol was found to be very similar to the trihexosan, $(C_6H_{10}O_5)_3$, obtained by Pictet. It comprises about 65% of the total dextrin content of the seedlings. The fraction precipitated by 40.0% alcohol is a complex mixture of higher dextrin aggregates, a report of which will be made later.

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[7] Pictet and Jahn, Helv. *Chim. Acta*, 5, 640 (1922).

[8] Sjöberg, Ber., 57, 1251 (1924).

[9] Pringsheim, *ibid.*, 57, 1581 (1924).

[10] Unpublished data of J. G. Dickson and K. P. Link.

Experimentation

Corn seedlings were grown at 24–28° by germinating them in soil, in the Wisconsin constant temperature soil tanks.[11] The seedlings, planted at a depth of 2.5 inches, were harvested when they reached the stage where the coleoptile ruptured the leaf sheath.[12] They were then removed from the soil, washed and separated from the remaining endosperm tissue. The method of killing plant tissue at 98°, followed by rapid drying at 65° in a current of air, previously reported by the writer, was used to preserve the tissue.[13] The dried tissue, containing approximately 6–8% of water was prepared for the chemical investigations in the identical manner used by the writer with other plant tissue.[14]

Extraction of Fat, Pigments, Waxy Constituents and Sugar.—Four kilos of the ground tissue was extracted in a large Soxhlet with ether for thirty-six hours and then with petroleum ether (b. p. 90–110°) for fifteen hours. After removing the fat solvents, the extraction was continued for twenty-four hours with 95.0% alcohol to remove the sugar present.

Extraction of Dextrins.—The fat, pigment and sugar-free residue was placed in a large bottle with 20 times its weight of 20.0% alcohol and extracted by shaking upon a machine for six days. The extraction was repeated for two days with a fresh portion of alcohol. No more dextrins could be removed with 20.0% alcohol after the second extraction. The large volume of 20.0% alcohol was then concentrated carefully in a vacuum of 15 mm. at 40° to one-seventh of the original volume. Alcohol (99.0%) was added until the concentration approximated 40.0%. The solution was then kept in an ice chamber at 2° for four days, during which time the separation of the dextrin fraction that gave a positive reaction with iodine was complete. After the precipitated dextrin was filtered, sufficient 99.0% alcohol was added to the filtrate to produce a concentration of 85.0%. On standing for five days at 2° the precipitation of the second dextrin was complete. The yield of the crude product was 72.0 g. This was purified by dissolving in water and reprecipitating with alcohol. After six reprecipitations the product was obtained as an amorphous snow-white powder, free from ash and nitrogen. The yield of the purified product was 63.0 grams.[15]

Properties and Analysis of the Dextrin.—The dextrin does not reduce Fehling's solution, gives no color with iodine and has a feeble insipid taste. It decomposes at 220–230" without melting. The specific rotation in water is $[\alpha]^{20}_{D}$, +163.6. The ultimate analysis showed C, 44.44; H, 6.19 (Pregl micro method); calcd. for $(C_6H_{10}O_5)_3$: C, 44.44; H, 6.21%. On hydrolysis in 2.5% sulfuric acid it was converted into glucose in 92.0% yields. The osazone prepared from the hydrolyzed solution showed m. p. 204–208°, the m. p. for glucosazone. The nono-acetyl derivative, $C_{36}H_{48}O_{24}$, prepared after the method of Pictet, showed m. p. 152–153°; $[\alpha]^{20}_{D}$, +125.9° in chloroform.

The dextrin (trihexosan) was converted into the monomethyl derivative, methoxyl content 17.40% (Zeisel–Pregl) in the manner employed by Kuhn and Zeise.[16] The

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[11] Jones, Johnson and Dickson, Wisconsin Agr. Expt. Sta., *Bull.*, 71 (1926).

[12] At this stage the seedlings are emerging from the soil. The photosynthesis of food materials has not begun. All the chemical constituents present in the seedlings are therefore derived from the embryo and endosperm reserves.

[13] Link, THIS JOURNAL, 47, 470 (1925).

[14] Link, *ibid.*, 45, 439 (1923).

[15] The product was dried first in 95.0%, then in 99.5%, alcohol. The alcohol was replaced by ether, which was in turn removed at 15 mm. pressure in a vacuum desiccator over calcium chloride.

[16] Kuhn and Zeise, Ber., 59, 2314 (1926).

monomethyl derivative gave no color with iodine and could not be saccharified with diastatic enzymes. Upon hydrolysis in 5% hydrochloric acid it gave 6-monomethylglucose, isolated as the osazone, m. p. 176–179°, identical with the figure given by Helferich and Becker.[17]

An attempt was made to determine the molecular weight of the unsubstituted product by the cryoscopic method, but consistent values could not be obtained. Using water as the solvent, the values found varied between 510 and 639. Pictet reported the molecular weight of 503 for the unsubstituted trihexosan and 871 for the mono-acetyl derivative. The molecular weight determinations of the mono-acetyl derivative varied between the values 820 to 960° with chloroform as the solvent and 790 to 980 with glacial acetic acid as the solvent.

Discussion

The properties and analyses of the dextrin isolated from the corn seedling indicate that it is quite comparable to the trihexosan, $(C_6H_{10}O_5)_3$, prepared by Pictet by the thermal depolymerization of potato starch in glycerin at 200–210°. It is prudent not to consider the dextrin from the corn seedling as strictly identical with the trihexosan of Pictet, since the molecular weight determinations are not in agreement with the figures reported by Pictet.[18]

The molecular weight determinations of polysaccharide compounds and their derivatives have long since been known to give contradictory results. Time and time again the chemist has been deceived by drawing rigid conclusions from molecular weight data obtained in the study of amorphous polysaccharide substances. The work of Karrer,[19] Bergmann,[20] Pringsheim,[21] Hess[22] and their co-workers has revealed the most unsuspected and unconquerable difficulties, due to the tendency of polysaccharide substances to form molecular aggregates through association. Molecular weight determinations of amorphous substances should be accepted with precaution, as Karrer has pointed out in his monograph.[23] Therein he states that he had failed to obtain the trihexosan of Pictet and the dihexosan of Pringsheim and Sjöberg in a true crystalline condition, as these workers had reported. Furthermore, Karrer questions the homogeneity of both the dihexosan and trihexosan. The argument is advanced that trihexosan can be hydrolyzed to maltose by enzymes, without the simultaneous formation of glucose, and that it can likewise be converted into acetobromo-

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[17] Helferich and Becker, *Ann.*, 440, 1 (1924).

[18] It is not known whether the thermal depolymerization of corn starch yields a trihexosan identical with the trihexosan from potato starch.

[19] Karrer, *Ergebnisse der Physiol.*, 20, 464 (1922).

[20] Bergmann, Knehe and Lippmann, *Ann.*, 458, 93 (1927); 449, 302 (1926); 452, 141 (1927).

[21] Pringsheim, *Naturwissenschaften*, 12, 360 (1924).

[22] Hess and Schultze, *Ann.*, 448, 114 (1926); 455, 84 (1927); 455, 198 (1927).

[23] Karrer, "Die Polymere Kohlenhydrate," Akademisches Verlagsgesellschaft, Leipzig, 1925, pp. 86–88.

maltose by the action of acetyl bromide, without the formation of acetobromoglucose. From these experiments Karrer concludes that the trihexosan, $(C_6H_{10}O_5)_3$, cannot be a three-membered glucose structure (that is, one molecule of glucose with one molecule of maltose), but that it must be a higher glucose polymer, which would yield maltose quantitatively upon hydrolysis and acetobromomaltose by the action of acetyl bromide. Karrer rejects the validity of the molecular weight determinations of the trihexosan and regards any conclusion drawn therefrom as presumptuous.

Pictet adhered to the belief that the trihexosan, $(C_6H_{10}O_5)_3$, represents the basal structural unit of the potato starch molecule, since it could be obtained in yields of the order of 90.0%. Sjoberg obtained both a dihexosan and a trihexosan from starch by enzymatic hydrolysis and concluded that the Pringsheim theory of the basal di- and trihexosan structure of starch was correct. According to this theory, the dihexosan is regarded as derived from the amylose and the trihexosan from the amylopectin of the starch grain. A dextrin comparable to dihexosan could not be isolated from the corn seedling. The dextrins present, besides the one closely related to Pictet's trihexosan, are of a higher molecular order.

Since the corn seedlings had not begun the photosynthetic process at the stage at which they were harvested, the dextrins in the tissue may be regarded as derived from one or both of two sources. They might have been translocated from the endosperm through the scutellum into the radicle and plumule—or they might have been synthesized from the sucrose present. Maltose appears to be absent from the radicle and plumule of the corn seedling at the stage of the rupturing of the leaf sheath by the coleoptile.

The chemical properties of the dextrin isolated (tabulated in Tables I and II) indicate that it is logical to regard it as a member of the starch dextrin series rather than of the cellulose dextrin series. Micheel,[24] one of Hess' co-workers, has recently isolated an amorphous trihexosan by the acetolysis of cellulose with hydrobromic acid and acetyl bromide. The physical constants and properties of the trihexosan isolated by Micheel indicate that it is not identical or related to the trihexosan obtained from starch.

It appears, therefore, that the dextrin isolated from the corn seedling represents a glucose polymer of the starch dextrin series, rather than of the cellulose dextrin series, and that it is not a polysaccharide substance directly used in the synthesis of the structural elements of the cell wall. It is possible that the dextrin is used as a respiratory material in the metabolism of the seedling.

In the following table the properties and physical constants of the dextrin isolated from the corn seedling are listed for comparison with those of

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[24] Micheel, Ann., 456, 69–86 (1927).

Pictet's trihexosan prepared from potato starch by thermal depolymerization and the Micheel–Hess trihexosan obtained from cotton cellulose by the action of hydrobromic acid and acetyl bromide.

TABLE I

COMPARISON OF PROPERTIES

Properties and constants	**Dextrin from corn seedlings (Link)**	**Trihexosan from potato starch (Pictet)**	**Trihexosan from cellulose (Micheel–Hess)**
Physical state	Amorph. white powder	Amorph. white powder[a]	Amorph. white powder
Soly. in water	Readily	Readily	Readily
M. p., °C.	Decomp. 220–230	Decomp. 230–232	Decomp. 184–189
Sp. rot. (water as solv.)	+163.6°	+162.2°	+90.5°
Mol. wt. (cryosc. meth., water as solv., calcd. for $(C_6H_{10}O_5)_3$, 486)	510–639	503.0	445[b]
Action on Fehling's soln.	None	None	None

[a] Reported as crystalline in the review by Pictet in Walton, "A Comprehensive Survey of Starch Chemistry," Chemical Catalog Co., New York, 1928. In the original, *Helv. Chimica Acta*, **5**, 640 (1922), as amorphous.

[b] Micheel and Hess state that their trihexosan and its acetyl derivative do not exhibit association properties.

The properties and constants for the corresponding nona-acetyl derivative are listed in Table II.

TABLE II

COMPARISON OF PROPERTIES

Properties and constants	**Nona-acetate, Link dextrin**	**Nona-acetate, Pictet trihexosan**	**Nona-acetate, Micheel-Hess trihexosan**
Physical state	Amorphous	Amorphous	Cryst. add. compds. with solns.
M. p., °C.	152–153	153–154	123–126
Sp. rot.	$125.9" in $CHCl_3$	+125.8–126.1° in glac. AcOH	+86.6° in $CHCl_3$
Mol. wt. (cryosc. meth., calcd. for $C_{36}H_{48}O_{24}$, 864)	820–960 in $CHCl_3$, 790–980 in glac. AcOH	871 in $CHCl_3$	834[a] in glac. AcOH

[a] Micheel and Hess state that their trihexosan and its acetyl derivative do not exhibit association properties.

In concluding the author wishes to acknowledge his indebtedness to Dr. James G. Dickson, of the Department of Plant Pathology, for advice and criticism received throughout the course of this investigation.

Summary

A dextrin has been isolated from the radicle and plumule of corn seedlings, which appears to be similar to the trihexosan, $(C_6H_{10}O_5)_3$, obtained

by the thermal depolymerization of potato starch. The dextrin comprises approximately 65% of the total dextrin content of the corn seedlings. Since the dextrin belongs to the starch dextrin series, it appears probable that it is a polysaccharide substance used in the respiratory process of the seedlings.

DEPARTMENT OF AGRICULTURAL CHEMISTRY
MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE POLYTECHNIC INSTITUTE OR BROOKLYN]

MONOARYLGUANIDINES. II. BENZOXAZOLEGUANIDINE[1]

BY G. B. L. SMITH, J. H. KANE[2] AND C. W. MASON[3]

RECEIVED MARCH 23, 1929 PUBLISHED AUGUST 7, 1929

Introduction

Since o-aminophenol reacts with organic compounds containing the nitrile group to form benzoxazoles,[4] it was thought that this type reaction might be employed as an additional confirmation of the cyanoguanidine formula of dicyandiamide.[5] Dicyandiamide was first prepared by Beilstein and Geuther,[6] and the present name was given to the compound by Haag.[7] In addition to the Bamberger formula three other possible structural configurations have been suggested.[8] The Bamberger α-cyanoguanidine formula, originally suggested with very little substantial proof, is now generally accepted, and probably the most convincing arguments for the correctness of this formula have been advanced by Hale and Vibrans,[9] who reviewed the literature concerning dicyandiamide and studied the product of the reaction between acetylacetone and dicyandiamide. Blair and Braham[10] believe that this structural configuration explains the formation of biguanide and guanidine salts when dicyandiamide is fused

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[1] This paper was presented at the Columbus meeting of the American Chemical Society, April 30–May 4, 1929.

[2] This paper is constructed from part of the thesis submitted by Mr. Kane in partial fulfilment of the requirements for the degree of Bachelor of Science in Chemistry at the Polytechnic Institute of Brooklyn in June, 1928.

[3] Assistant Professor of Chemical Microscopy at Cornell University.

[4] (a) Skraup, *Ann.*, **419**, 75 (1919); (b) Wheeler, *Am. Chem. J.*, 17, 400 (1895).

[5] Suggested by Bamberger, Ber., 16, 1074 (1883).

[6] Beilstein and Geuther, *Ann.*, **108**, 99 (1858); 123, 241 (1862).

[7] Haag, *ibid.*, 122, 22 (1862).

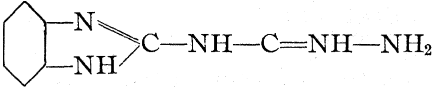
[8] (a) Strecker, "Lehrbuch der Organischen Chemie," 5th ed., p. 637, through Hallwachs, *Ann.*, 153, 293 (1870); (b) Klason, *J. prakt. Chem.*, [2] 33, 126 (1886); (c) Pohl, *ibid.*, [2] 77, 533 (1908).

[9] Hale and Vibrans, THIS JOURNAL, 40, 1046 (1918).

[10] Blair and Braham, *ibid.*, 44, 2342 (1922).

with ammonium salts. On the other hand, Werner and Bell[11] have not accepted this formula and more recently Hart,[12] a student of E. C. Franklin, assumed the Pohl @-cyanoguanidine formula in writing the equation for the reduction of dicyandiazide to dicyandiamide.[13]

In addition to the condensation of o-aminophenol with a nitrile group, benzoxazoles may be formed by condensation of o-aminophenol with a carboxyl group[14] or with an acid amide,[4a] and benzimidazoles may be prepared by substituting o-phenylenediamine for o-aminophenol. Ziegelbauer[15] and Pellizzari[16] have prepared a compound which they called o-phenylenebiguanide by the interaction of *o*-phenylenediamine and dicyandiamide and Pellizzari assigned the formula

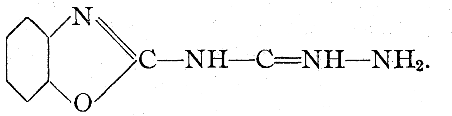


to this compound.[17]

This reaction is of peculiar interest in connection with the present investigation as it also gives simple proof of the presence of the nitrile group in the dicyandiamide molecule.

Reaction between o-Aminophenol and Dicyandiamide.—Ammonia is copiously liberated when *o*-aminophenol and dicyandiamide in molecular proportions are fused. When heated under a reflux in an alcoholic solution of hydrochloric acid, they react to form the hydrochloride salt of a new base. This salt may be isolated by crystallization from the alcoholic solution; when dissolved in water and treated with a solution of sodium hydroxide, the free base is obtained. The mother liquor from the original reaction gives ammonia on treatment with an excess of a solution of sodium hydroxide and practically one mole for each mole of reacting substances was obtained. The base was found to have the formula $C_8H_8N_4O\cdot H_2O$, and several monobasic salts of $C_8H_8N_4O$ were prepared.

The following evidence is offered as proof that this substance is benzoxazoleguanidine,



(1) The base does not give reactions characteristic of the phenylhydroxy or phenylamino

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[11] Werner and Bell, *J. Chem. Soc.*, 117, 1133 (1920); 121, 1790 (1922).

[12] Hart, THIS JOURNAL, 50, 1922 (1928).

[13] Attention is called to the possibility of an intramolecular rearrangement to the Bamberger formula in this reaction.

[14] Ladenburg, *Ber.*, 9, 1524 (1876).

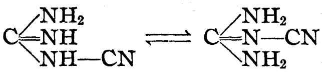
[15] Ziegelbauer, *Monatsh.*, 17, 653 (1896).

[16] Pellizzari, *Gazz. chim. ital.*, I, **51**, 89, 140 (1921); see C. *A.*, 15, 3076, 3078 (1921).

[17] The authors of this paper prefer to call the substance benzimidazoleguanidine. The preparation has been repeated in this Laboratory and a new sulfate, $C_8H_9N_5\cdot H_2SO_4\cdot 2H_2O$ has been prepared; H. A. Roth, "Thesis," Polytechnic Institute of Brooklyn, 1928.

groups. (2) A diacetyl derivative has been prepared.[18] (3) A quaternary methyl iodide derivative has been prepared.[19]

This reaction between o-aminophenol and dicyandiamide to form benzoxazoleguanidine gives direct positive evidence of the presence of the nitrile group in the dicyandiamide molecule. It also confirms the conclusion of Pellizzari regarding the structure of o-phenylenebiguanide (benzimidazolguanidine). All these results may be explained by assuming either the Bamberger or the Pohl formula. It is indeed highly probable that dicyandiamide is a tautomeric compound and, therefore, an equilibrium product which may be represented by the following



$$\mathrm{C}\begin{cases}\mathrm{NH_2}\\ \mathrm{=NH}\\ \mathrm{NH{-}CN}\end{cases} \rightleftharpoons \mathrm{C}\begin{cases}\mathrm{NH_2}\\ \mathrm{=N{-}CN}\\ \mathrm{NH_2}\end{cases}$$

The facts here presented are entirely consistent with this view.

Experimental

Crude Benzoxazoleguanidine Hydrochloride.—One hundred grams of *o*-aminophenol[20] was dissolved in a mixture of 100 cc. of concentrated hydrochloric acid and 100 cc. of 95% alcohol and heated to boiling under a reflux for fifteen minutes. Eighty grams of dicyandiamide[21] was added and the heating was continued for two hours. On cooling crystals formed which were separated by filtration and a second crop was secured by concentration of the mother liquor to half volume. The product thus obtained was dark in color and was used for the subsequent preparation of the base; yield, 130 g.

Ammonia Produced in the Reaction.—An aliquot portion of the mother liquor from the above reaction was treated with a concentrated solution of sodium hydroxide and the liberated ammonia was distilled into an excess of standard acid. The ammonia was determined in the usual manner and 91% of the theoretical (corresponding to 1 mole of NH_3 for each mole of dicyandiamide and o-aminophenol) was recovered.

Benzoxazoleguanidine Monohydrate (Base).—Fifty grams of crude benzoxazoleguanidine hydrochloride was dissolved in 300 cc. of boiling water and 13 g. of potassium hydroxide dissolved in 50 cc. of water was added. The base precipitated immediately and after cooling was filtered, washed with cold water and dried; yield, 45 g. This procedure gives a product somewhat yellow in color, but purification may be effected by dissolving in hot water, treating with vegetable charcoal and recrystallizing, or by dissolving in alcohol and pouring into a large volume of cold water.

Benzoxazoleguanidine monohydrate forms glistening pearly very pale yellow platelets. It is very soluble in alcohol and sparingly soluble in water. Molecular weight determinations of the dehydrated base in acetone by elevation of the boiling point yielded results varying from 170–180. Neither alcoholic nor aqueous solutions of the base gave

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[18] The fact that a triacetyl derivative could not be prepared may be attributable to steric hindrance due to the electronegative character of the benzoxazole ring. The electronegative character of this compound is demonstrated by its low activity as an accelerator of vulcanization of rubber; Smith and Wise, *Ind. Eng. Chem.*, 20, 298 (1928).

[19] This reaction is characteristic of benzoxazoles; Fischer, *J. prakt. Chem.*, [2] 73, 436 (1906).

[20] Practical grade, obtained from the Eastman Kodak Co.

[21] Obtained from the American Cyanamide Co.

any coloration with a solution of ferric chloride, showing thereby the absence of the phenylhydroxy group. Also, an aqueous suspension of lead dioxide in acetic acid gave no color reaction with solutions of benzoxazoleguanidine, indicating the absence of a primary amino group attached to the benzene nucleus. o-Aminophenol gave positive color reactions in each case.

Salts of Benzoxazoleguanidine.—Benzoxazoleguanidine nitrate, sulfate, hydrochloride and picrate were prepared by dissolving 10 g. of the base in the least possible amount of boiling water and treating immediately with a slight excess of the respective acid. The salts are all sparingly soluble in water and crystallized when the solutions were cooled. The salts of the strong acids hydrolyzed in aqueous solution and could be titrated with a standard aikali using phenolphthalein as indicator. Analyses recorded with the exception of the nitrate are all gravimetric determinations by standard methods. The analytical and other data for the base and salts are given in the accompanying table.

TABLE I

ANALYTICAL AND OTHER DATA

Compound	Analyses, %	Calcd.	Found	Solubility G./100 g. of H_2O	M. p., °C.
Base				0.0303— 15°	182–184
(Monohydrate)	C,	49.40	49.47, 49.30	.0383— 20°	
	H,	5.19	5.19, 5.19	.0821— 30°	
	N,	28.88	29 20, 28.90	.1608— 50°	
	H_2O,	9.30	9 70, 9.80	,3740— 70°	
				1 5677— 90°	
				2.7524—100°	
Hydrochloride	HCl,	17 09	17 10, 17.19	1.6160—20.5"	254–255
Sulfate	H_2SO_4,	21.67	22.03, 22 08	0 0918—20.5°	280–281
Nitrate	HNO_3,	26 35	26 34, 26.34	.2405—20.5°	219–220
Picrate	N,	24.10	23.81, 23.90	.0184—20.5°	247–248

Diacetylbenzoxazoleguanidine.—Three grams of benzoxazoleguanidine, dissolved in alcohol, was heated with 15 g. of acetic anhydride for forty minutes. The solution was cooled and then poured into cold water and diacetylbenzoxazoleguanidine precipitated; m. p. 209–210°.

Anal. Subs., 0.5000, 0.5000: 7.81, 7.70 cc. of 1.0 *N* HCl. Calcd.: N, 21.54. Found: N, 21.87, 21.54.

Iodide of Quaternary Methylbenzoxazoleguanidine.—Benzoxazoleguanidine was heated with an excess of methyl iodide under a reflux for four hours. Alcohol was added to form a clear solution and the heating was continued for three hours. The solution was cooled and poured into ether and a crystalline product precipitated; m. p. 192–194".

Anal. Subs. 0.5000, 0.5000: 15.64, 15.52 cc. of 0.1 N $AgNO_3$. Calcd.: I, 39.90. Found: I, 39.7, 39.4.

Microscopical Notes

Base (Monohydrate).—Recrystallized from hot water, by cooling, or from alcohol by dilution with water, the base gave thin, lath-shaped forms, single or in forked and curving clusters; ends jagged, or rarely oblique, with angles of about 70 or 56°; double refraction strong, with parallel extinction and positive elongation edgewise and flatwise. The index of refraction for vibrations crosswise of the crystals is 1.635; lengthwise of the crystals, 1.495. The axial plane is apparently parallel to the elongation.

Recrystallized from 95% alcohol by evaporation, the crystals are the same phase as above, for they may grow directly on them, with no optical discontinuity; six-sided plates, in coffin shapes or in obtuse-ended forms, are common, together with elongated trapezoidal plates. The angles and optical orientation of these crystals indicate that they are identical with those obtained by recrystallization from water, but with somewhat different "habit." Their plane of symmetry corresponds to the transverse plane of the long lath-shaped forms. The six-sided plates show symmetrical extinction flatwise and edgewise in one position. The other edge view exhibits oblique extinction, about 38°, and since the axial plane is inclined to the plane of the plates in a similar direction, the crystals may be assigned to the monoclinic system. The refractive index for vibrations crosswise of the coffin-shaped forms is 1.495; lengthwise, 1.635. The double refraction is probably positive. When heated dry, the crystals become opaque and melt. The melt supercools markedly but eventually crystallizes. Probably dehydration is not complete by melting without continued heating, since the crystals of the hydrate may grow into the melt.

Hydrochloride.—Recrystallized from hot water by cooling, lath-shaped forms, single or clustered, appear first; some show ends obliquely truncated (60°). Their double refraction is strong, with an extinction of about 25° to the long direction of the plates and nearly parallel to their oblique ends. The axial plane is nearly perpendicular to these end faces and corresponds to the lower refractive index (1.490) for this view of the crystals; the other refractive index is about 1.61. 2 V is large, $r < v$, and the crystals are probably negative. They probably belong to the triclinic system. As crystallization proceeds further, other more complex crystals make their appearance as rhomb-shaped plates, generally rounded, and often with the acute angles truncated. They are not single crystals, but are lamellar aggregates or twins. Their polarization colors are anomalous, and they do not extinguish but change hue when rotated between crossed nicols. Their interference figures are very distinctive and indicative of their composite nature; nearly straight dark bars appear alternately in the two 45° positions, but do not rotate.

Sulfate.—When recrystallized from hot water by cooling, the compound forms radiating clusters of strongly curving delicate plates, and opaque mossy rosets. Crystals formed more slowly are lath-shaped, but with poorly defined end faces. They show oblique extinction, the maximum angle being 25'. Their double refraction is strong, with only positive elongation observed.

Recrystallized from sulfuric acid (about 10%), trichiten rosets appear, and on further concentration, rhomb-shaped plates. Laminated growths are frequent. The trichiten rosets are probably identical with the phase described above, but the rhomb-shaped plates, separating from more concentrated acid, are probably the acid salt. By varying the acid concentration in the drop, either phase can be made to grow at the expense of the other. The acid sulfate crystallizes in tablets with obtusely pointed ends, the terminal angles being about 130'. Actually they are monoclinic prisms flattened in the direction of the C axis, the plane of symmetry being crosswise of the longer tablets and parallel to the acute diagonal of the shorter, rhomb-shaped ones. Multiple lamellar twinning in the basal plane is common but does not appear to alter the symmetry of the crystals as a whole. Birefringence is strong, positive, with 2 V large and $r < v$, or else inclined dispersion. Interference figures show only one of the optic axes, which lie in the plane of symmetry of the crystals with the acute bisectrix inclined to the basal plane of the tablets. The crystals may be assigned to the monoclinic system.

Nitrate.—It recrystallizes from hot water in sheaves and rosets of tiny rounded platelets, strongly birefringent.

Picrate.—Recrystallized from hot water, it gives fine thin blade-like and leafy crystals, strongly birefringent, pleochroic in two shades of yellow. The faces and angles are not well defined.

Summary

The reaction between o-aminophenol and dicyandiamide results in the formation of benzoxazoleguanidine. This reaction gives direct proof of the presence of the nitrile group in the dicyandiamide molecule. The properties of a number of derivatives of benzoxazoleguanidine are described.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 217]

THE SYNTHESIS OF THE ISOMERIC 2-BUTENES[1]

BY WILLIAM G. YOUNG,[2] ROBERT T. DILLON[2] AND HOWARD J. LUCAS[3]

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Introduction

It was necessary to prepare the *cis* and *trans* forms of 2-butene in a pure condition before a satisfactory method of analysis involving the three normal butenes could be developed. The synthesis of 1-butene has already been reported.[4]

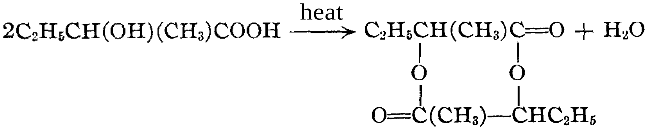
The preparation of the isomeric forms of 2-butene from the two naturally occurring a-methylcrotonic acids, *viz.*, angelic and tiglic acids, has been described by Wislicenus and his co-workers.[5] Since angelic acid is the less stable form, rearranging under the influence of heat or light to the more stable tiglic acid, it is desirable to use a synthetic method which produces as large a yield of angelic acid as possible. The thermal decomposition of a-methyl-a-hydroxybutyric acid[6] serves this purpose. In this work the desired hydrocarbons have been synthesized from methylethyl ketone by the reactions shown in Equations 1, 2, 3, 6 and 7.

$$CH_3CH_2COCH_3 + NaHSO_3 + NaCN \longrightarrow CH_3CH_2CH(OH)(CH_3)CN + Na_2SO_3 \quad (1)$$

$$CH_3CH_2CH(OH)(CH_3)CN + 2H_2O + HCl \longrightarrow CH_3CH_2CH(OH)(CH_3)COOH + NH_4Cl \quad (2)$$

$$CH_3CH_2CH(OH)(CH_3)COOH \xrightarrow{\text{heat}} \underset{\text{angelic acid, tiglic acid}}{CH_3CH{=}C(CH_3)COOH} + H_2O \quad (3)$$

$$CH_3CH_2CH(OH)(CH_3)COOH \xrightarrow{\text{heat}} CH_2{=}C(C_2H_5)COOH + H_2O \quad (4)$$



$$2C_2H_5CH(OH)(CH_3)COOH \xrightarrow{\text{heat}} \begin{array}{l} C_2H_5CH(CH_3)C{=}O \\ \qquad\qquad\;\; | \qquad\;\; | \\ \qquad\qquad\;\; O \qquad O \\ \qquad\qquad\;\; | \qquad\;\; | \\ \qquad O{=}C(CH_3){-}CHC_2H_5 \end{array} + H_2O \quad (5)$$

$$CH_3CH{=}C(CH_3)COOH + HI \longrightarrow CH_3CHICH(CH_3)COOH \quad (6)$$

$$CH_3CHICH(CH_3)COOH + Na_2CO_3 \longrightarrow CH_3CH{=}CHCH_3 + NaI + NaHCO_3 + CO_2 + H_2O \quad (7)$$

In agreement with Wislicenus and his co-workers we obtained the higher boiling isomer from angelic acid and the lower boiling from tiglic acid,

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[1] This paper contains results obtained in an investigation listed as Project No. 14 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] American Petroleum Institute Research Assistant, 1927–1928.

[3] Director, Project No. 14.

[4] Lucas and Dillon, THIS JOURNAL, 50,1460 (1928).

[5] Wislicenus, Talbot, Henze and Schmidt, *Ann.*, **313,** 207–250 (1909).

[6] Blaise, *Ann. chim. phys.*, [8] 11, 116 (1907).

but the boiling points of our products were somewhat different, being +2.95–3.05° and +0.30–0.40° instead of +2.0–2.7° and +1.0–1.5°, respectively. These workers assigned the *cis* structure to the lower boiling and the *trans* structure to the higher boiling hydrocarbon, whereas Pfeiffer[7] claimed just the reverse. We prefer Pfeiffer's structures and have used them in this paper. We hope definitely to establish the structures by measuring the electric moments of the hydrocarbons and of their dibromides. With bromine at 0° the *cis* hydrocarbon yields a dibromide, b. p. 75.6–75.8° (corr.) at 50.0 mm., and the *trans* yields a dibromide, b. p. 72.7–72.9° (corr.) at 50-mm. pressure. Tentatively we have assumed that the higher boiling dibromide is the racemic and the lower boiling is the meso form, since the recent work of Terry and Eichelberger[8] indicates that when bromine adds to the olefin bond the addition is *trans*. Further confirmation is shown by the fact that in the reaction of these dibromides with potassium iodide in methanol the meso isomer has the higher reaction rate. This agrees with the observation of C. van Duin[9] who found that the meso-dibromosuccinic acid has a higher reaction rate with potassium iodide in 75% ethanol than the racemic.

General Discussion of the Method

In the cyanhydrin reaction (Equation 1) best results were obtained when the procedure usually employed for other compounds[10,11] was modified by using a minimum quantity of water, changing the order in which the chemicals were added and maintaining a temperature of 35° during the reaction. The hydrolysis of the cyanhydrin (Equation 2) should be carried out at temperatures below 90°, since the resulting acid sublimes rapidly at temperatures above 90".

It is absolutely essential to obtain the α-hydroxy-α-methylbutyric acid in a high degree of purity, since Blaise[6] has shown that when traces of hydrogen chloride are present in the hydroxy acid, the yield of angelic acid is very small. This is due to the catalytic effect of hydrogen chloride upon the rate with which angelic acid is converted into the more stable tiglic acid. In this work a very pure halogen-free product, having a melting point higher than any previously reported, was obtained by a single distillation at reduced pressure. This procedure is superior to the previous tedious method of crystallization from benzene, which must be followed by two weeks' desiccation over solid sodium hydroxide. The yields obtained by different procedures are shown in Table I.

[7] Pfeiffer, *Z. physik. Chem.*, 48, 58 (1904).

[8] Terry and Eichelberger, THIS JOURNAL, 47, 1067 (1925).

[9] C. van Duin, *Rec. trav. chim.*, 45, 345 (1926).

[10] Cumming, Hopper and Wheeler, "Systematic Organic Chemistry," D. Van Nostrand Co., New York, 1925. Preparation 82, p. 151.

[11] "Organic Syntheses," John Wiley and Sons, New York, 1926, Vol. VI, p. 58.

TABLE I

COMPARATIVE YIELDS OF α-HYDROXY-α-METHYLBUTYRIC ACID

Expt.	NaCN, g.	$NaHSO_3$, g.	Methyl ethyl ketone, g.	Crude cyanhydrin g.	α-Hydroxy-a-methyl butyric acid, g.	Yield, %
5	150	315	216	294	168	47.4[a]
6	165	380	216	314	158	44.5[a]
9	53	126	72	90	56	47.5[b]
11	165	380	216	296	221	62.5[c]
13	165	380	216	320	228	64.5[c]
14	165	380	216	317	219	62.0[c]

[a] Method from "Systematic Organic Chemistry," ref. 10.
[b] Method from "Organic Syntheses," ref. 11.
[c] Method described in this paper.

In the decomposition of the hydroxy acid (Equations 3, 4 and 5) best results were obtained by removing the low-boiling decomposition products from the reaction flask as soon as they were formed. The purification of the resulting angelic and tiglic acids involves a separation from a-ethylacrylic acid, not previously reported as a product of this decomposition (Equation 4). The effect of temperature upon the rate with which angelic acid is converted into tiglic necessitates low-pressure distillations with small quantities of material. By a combination of fractional crystallization and fractional distillation at 12 mm. through a bead column 50 cm. long, angelic and tiglic acids were obtained in a high degree of purity with yields of 20% each. This corresponds to a 40% conversion of the hydroxy acid into the desired products, which is a 6% higher yield than that reported by Blaise.[6]

The reaction of hydrogen iodide[12] with tiglic acid in chloroform solution (Equation 6) proceeded satisfactorily, but the conversion of angelic acid into its hydriodide was difficult since the addition compound slowly isomerized into tiglic acid hydriodide. This change was markedly accelerated by iodine, which must not be present in the chloroform solution of hydrogen iodide. Even though the reaction flask was kept in the dark at 3° during the seven days required for the completion of the reaction, some iodine was formed. The addition of some molecular silver removed the iodine and led to higher yields of the angelic acid derivative. Great care was taken to obtain these two hydrogen iodide addition compounds in a high state of purity since contamination of either one with some of its isomer would result in a mixture of butenes instead of a pure substance.

The decomposition of the above iodo acids into the isomeric 2-butenes (Equation 7) was done in sodium carbonate solution.[5] After the materials were mixed at 5°, gas evolution took place in three distinct stages. As the temperature was slowly raised to 20–30°, carbon dioxide was evolved.

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[12] Prepared by the method of Dillon and Young, THIS JOURNAL, 51, 2389 (1929).

This was removed from the gas stream by absorption in sodium hydroxide solution. Apparently little or no butene was formed during this first stage. At higher temperatures butene but no carbon dioxide was evolved. Finally, above 60°, the carbon dioxide resulting from the decomposition of the sodium bicarbonate swept the apparatus free from butene. The angelic acid derivative was the more stable, as shown by the fact that the second stage started at 30°, whereas the corresponding temperature was 20° for the tiglic acid compound. A rapid increase in temperature during the decomposition of the angelic acid hydriodide resulted in a yield of butene 20% higher than that previously reported. This result was anticipated since it was assumed that, of the two possible reactions, decomposition and hydrolysis, the former would have the greater temperature coefficient. The yields obtained at the different steps and the physical constants of the various products are shown in Table II.

TABLE II

YIELDS AND PHYSICAL CONSTANTS OF COMPOUNDS

Substance	M. p., °C. (corr.)	B. p., °C. (corr.)	Density *in vacuo*	Refractive index	Yield, %	Overall yield, %
1 a-Hydroxy-u-methyl-butyric acid	72.5	118 (13 0 mm.), 117 (12.5 mm.), 116 (12 0 mm), 104 5 (7 0 mm.), 93 (2 3 mm.)	....	....	63.0	63.0
2 Angelic acid	45 0–45 5	85.5–87 5 (12–13 mm.)			20 0	12.6
3 Tiglic acid	63 5–64 0	95 0–96 0 (11 5 mm)			20 0	12 6
4 Angelic acid hydriodide	57 9–58.5	....	....	....	44.5	5 3
5 Tiglic acid hydriodide	86.2–86.3	....	....	....	7 4 0	8 9
6 Higher-boiling 2-butene from 4 (cis)	...	+2 95–3 05 at 746 mm.	....	....	65.4	3.4
7 Lower-boiling 2-butene from 5 (trans)	...	$0.3–0.4 at 744 mm.	....	....	84 0	7 5
8 Higher-boiling 2,3-dibromobutane from 6 (racemic)	...	75 6–75 8 at 50 0 mm.	$d_4^{20} = 1\ 7916$ $d_4^{25} = 1\ 7836$	$n_D^{20} = 1.5147$ $n_D^{25} = 1\ 5125$	95 5	3.2
9 Lower-boiling 2,3-dibromobutane from 7 (*meso*)	...	72.7–72.9at50.0 mm.	$d_4^{20} = 1.7829$ $d_4^{25} = 1.7747$	$n_D^{20} = 1.5116$ $n_D^{25} = 1\ 5092$	90.0	6 7

Experimental

α-Hydroxy-α-methylbutyric Acid.—This acid was obtained through the cyanhydrin reaction from methylethyl ketone. Crude methylethyl ketone, b. p. 72–80", was distilled in a 90-cm. bead column and the fraction distilling at 78–80' was used. In a 3-necked, 3-liter flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel were placed 400 g. of cracked ice, 50 g. of water, 165 g. (3.2 moles) of 95% sodium cyanide and 216 g. (3.0 moles) of methylethyl ketone, b. p. 78–80'. While the solution was being vigorously stirred, 380 g. of sodium metabisulfite (equivalent to 4.0 moles of sodium bisulfite) in 480 g. of water was introduced from the dropping funnel during the course of ten to fifteen minutes. When all but about one-quarter of the solution had been added, the temperature had risen to 35°. A cooling bath of ice and water was then placed outside the flask and a temperature of 30–40° was maintained for ten minutes after the last of the bisulfite had been added. By this time the reaction was finished. The mixture was cooled to 0°, at which temperature the solubility of the cyanhydrin in the salt solution is negligible. The oily cyanhydrin was poured off from the mushy salt layer, 50–100 ml. of water was added to the latter and the additional oil which rose to the top on shaking was again poured off. The crude cyanhydrin, 320–330 g., was hydrolyzed by heating at 90–100° under a reflux cooler with 400 g. of C. P. concd. hydrochloric acid. It was not advisable to heat the solution above 100°, since considerable hydrogen chloride and a-hydroxy-a-methylbutyric acid was lost by volatilization. At the end of seven hours the reaction was usually complete. The solution was cooled to room temperature and without removal of the large amount of ammonium chloride, 100 g. of hydrated sodium sulfate was added. This effects a marked decrease in the concentration of the hydrochloric acid, which is largely converted into sodium hydrogen sulfate and sodium chloride. The solution was cooled to −15° and the mixture of salts was filtered off. The organic acid was not affected by this treatment since its ionization constant is weaker than the second ionization constant of sulfuric acid. Unless the greater part of the hydrochloric acid was removed, the mutual solubilities of this solution and ether were so large that a considerable amount of water and hydrochloric acid dissolved. However, by the procedure adopted a satisfactory extraction of the hydroxy acid by ether could be made. The ether solution was dried with anhydrous sodium sulfate, the ether was distilled off and the α-hydroxy-α-methylbutyric acid was purified by distillation at low pressures. The acid may also be purified by crystallization from petroleum ether at −15°, but this is a more laborious and less satisfactory process since some hydrogen chloride remains in the product. The yield by the distillation method was 64.5% and the material melted at 72.5° (corr.).[13] In Table 1 a comparison is made of the yields obtained by different methods.

Angelic and Tiglic Acids.—The decomposition of α-hydroxy-α-methylbutyric acid was accomplished by slowly heating approximately 100–125 g. in a 250-ml. round-bottomed distilling flask provided with a 75-mm. bead column in the neck. At a slow rate of heating the decomposition products came over at 150–190°, but if the heating was too rapid considerable hydroxy acid would distil over and the temperature would rise above 190°. It was therefore necessary to heat slowly for a period of one and one-half to three hours in order to allow the slow reaction of decomposition to take place. As soon as no more water distilled, the temperature was raised to 210°, the receiver was changed, and the temperature carried to 240°. A small amount of undecomposed hydroxy acid came over at 210–215°, and considerable lactide at 235–240°. The latter represents 20–25% of the original material. The first fraction, approximately 100 cc., consisted of two phases of approximately equal densities. A separation of the desired unsaturated acids from dissolved water and from the water phase was conveniently accomplished by adding 50 ml. of petroleum ether to 200 ml. of the first distillate (from two decomposition experiments). The petroleum ether solution was dried with anhydrous sodium sulfate and the solvent was distilled off. No attempt was made to isolate any methyl ethyl ketone present. The residue of unsaturated acids was fractionally distilled at 12 mm. through a 50-cm. bead column. The results of the first distillation, as shown in Table III, indicate that a satisfactory separation had been made. After a second distillation at 12-mm. pressure the two main fractions were cooled. Solid angelic and tiglic acids separated out from the respective fractions and were filtered off on a platinum cone from the mother liquor, which was again fractionated.

The angelic and tiglic acids were obtained in a high state of purity by this procedure. The constants are listed in Table II.

From the fraction boiling below angelic acid, a-ethylacrylic acid, m. p. −16°, has been isolated. This material, which has not previously been reported as a product of this decomposition, represents 11% of the original hydroxy acid.

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[13] Boecking, *Ann.*, 104, 18 (1880), reported 66° and 68".

TABLE III

UNSATURATED ACIDS FROM DECOMPOSITION OF α-HYDROXY-α-METHYLBUTYRIC ACID; RESULT OF FIRST FRACTIONATION

Fraction	Material	B. p., °C. (corr.)	Press., mm.	Yield, %
1	α-Ethylacrylic acid	76.5–83°	12	11.0
2	α-Ethylacrylic acid and angelic acid	83–85	12	2.0
3	Angelic acid	85–87.5	12	25.0
4	Angelic acid and tiglic acid	87.5–94	12	5.8
5	Tiglic acid	94–96	12	17.0
6	Same and α-hydroxy-α-methylbutyric acid	96–115	12	2.0

The Hydriodides of Angelic and Tiglic Acids.—The addition of hydrogen iodide to the unsaturated acids was carried out according to the general method of Talbot.[5] Since this operation requires careful manipulation, the details of which are not mentioned by Talbot, it is desirable that the procedure developed in carrying out this step be described in detail.

An anhydrous solution of hydrogen iodide (0.6–0.7 N) in chloroform was made by passing pure, anhydrous hydrogen iodide[12] into 700 ml. of dry chloroform contained in a 2-liter pyrex distilling flask provided with a ground-glass stopper carrying an inlet tube reaching nearly to the bottom. The chloroform was kept at −15° and the side arm, which constituted the outlet tube, was provided with a drying tube containing phosphorus pentoxide. The concentration of hydrogen iodide was determined at intervals by titrating 2.00-ml. portions against 0.115 *N* NaOH. As soon as the required amount of hydrogen iodide was in solution (53.7–57.7 g.), the unsaturated acid (27.0–29.0 g., dissolved in chloroform) and 1 g. of molecular silver were quickly added. The molal ratio of hydriodic acid to the organic acid should not be less than 1.5 to 1. The outlet tubes of the flask were sealed off in a flame and the ground-glass stopper was tied in and coated with sealing wax. The flask was placed in the dark in an ice box and kept at 3° for seven days. It was then cooled to −15°, the side arm opened, the inlet tube removed and a capillary tube inserted in its place. The flask was heated by a water-bath at 30° and the chloroform was distilled at 20-mm. pressure. Low-temperature distillation was desirable since the decomposition of hydriodic acid and the change of the angelic to the tiglic acid derivative must be kept at a minimum. The residue was extracted at 30–35° with the least possible amount of petroleum ether, b. p. 40–60°, filtered to remove silver iodide and the filtrate was cooled to −15°. The crystalline hydriodide obtained by this procedure was pure when tiglic acid was the starting material but was a mixture when angelic acid was used. In the latter case the mixture contained large quantities of the stable tiglic acid hydriodide. This impure product was extracted twice at room temperature with 5-ml. portions of the petroleum ether and then dissolved at 30–35° in 20 ml. of the solvent. This solution was cooled and three crops of crystals were removed as the cooling progressed. Pure angelic acid hydriodide, m. p. 57.5–58.5°, constituted the first two crops, but the third crop and likewise the material obtained from the crystallization of the 5-cc. extractions were mixtures, as shown by the melting range of 39–52'. Although a small amount of the pure angelic acid hydriodide can be obtained by working up this crude material, it is not practicable to do so.

The Isomeric 2-Butenes.—The butenes were generated in a 3-necked, 3-liter flask provided with a mechanical stirrer, a dropping funnel and an outlet tube. To the latter were attached in series a spiral washing bottle containing aqueous sodium hydroxide for removing carbon dioxide, a calcium chloride drying tube, a receiving tube surrounded by an ice–hydrochloric acid bath at −30 to −35°, a specially designed flask containing bromine for absorbing any uncondensed butene and a drying tube of calcium chloride.

The reaction flask was immersed in a vessel of ice water, **71.5** g. **(0.314** mole) of the angelic or tiglic acid hydriodide was placed in the flask and **26.6** g. **(0.25** mole) of sodium carbonate dissolved in **650** ml. of water at **5°** was rapidly added through the dropping funnel. The liquid was stirred and the temperature of the bath was slowly raised. **A** lively evolution of carbon dioxide took place at 10° in the case of the tiglic acid and at 15° in the case of the angelic acid derivative. The temperature of the bath was increased as fast as the absorber would take care of the carbon dioxide. This corresponds to a rate of **20** to 30° per hour until 45–50° was reached. At 20° the gas from the tiglic solution and at 30° that from the angelic solution began to pass the absorber, and soon afterward the evolved gas seemed to be nearly pure butene. The temperature was increased more rapidly above 45° since the gas evolution had dropped off. At **65–70°** the evolution of carbon dioxide was again rapid and swept the residual butene into the receiver. Practically complete condensation of the butene **was** accomplished since not more than 1 ml. of dibromobutane was recovered from the bromine absorption flask.

When these hydrocarbons were separately distilled in the apparatus especially designed for this purpose, each distilled completely over a temperature range of 0.1°, as shown in Table II.

The Isomeric 2,3-Dibromobutanes.—These were prepared by slowly distilling the pure butenes into an all-glass reaction flask kept at −15° and adding from time to time small amounts of bromine. After the formation of the first quantity of dibromide the butene was always kept slightly in excess in order to avoid the formation of tribromides. At the end of the reaction, a slight excess of bromine was added to remove the last traces of butene. The products were immediately washed with dilute sodium bisulfite solution, sodium bicarbonate solution and water and were then dried with anhydrous calcium chloride. They were fractionally distilled at 50-mm. pressure in order to avoid the isomeric change which Faworsky[14] noted at more elevated temperatures. The small distillation range of each of the dibromides (Table II) indicates that a single substance and not a mixture of isomers is formed in each case.

Summary

Starting with methyl ethyl ketone, the cis- and trans-2-butenes have been synthesized in a high state of purity.

Necessary details are given for the preparation and purification of the following intermediate compounds: α-hydroxy-α-methylbutyric acid, angelic acid, tiglic acid, angelic acid hydriodide, tiglic acid hydriodide, the isomeric 2-butenes and the corresponding dibromobutanes.

PASADENA, CALIFORNIA

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[14] Faworsky, *Ann.*, 354, **325** (1907).

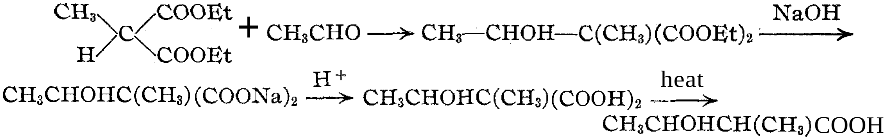
[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 218]

THE CONDENSATION OF ACETALDEHYDE WITH METHYLMALONIC ESTER. METHYLATIONS WITH METHYL BROMIDE

BY HOWARD J. LUCAS AND WILLIAM G. YOUNG[1]

RECEIVED APRIL 3, 1929 PUBLISHED AUGUST 7, 1929

In developing a method for synthesizing the isomeric 2-butenes, it was thought that the decomposition of β-hydroxy-α-methylbutyric acid might give a yield of the unsaturated angelic and tiglic acids higher than that which was obtained by the decomposition of or-hydroxy-a-methylbutyric acid. The attempt was therefore made to synthesize the β-hydroxy acid from methylmalonic ester through the following steps



$$(CH_3)(H)C(COOEt)_2 + CH_3CHO \longrightarrow CH_3\text{—}CHOH\text{—}C(CH_3)(COOEt)_2 \xrightarrow{NaOH}$$

$$CH_3CHOHC(CH_3)(COONa)_2 \xrightarrow{H^+} CH_3CHOHC(CH_3)(COOH)_2 \xrightarrow{heat} CH_3CHOHCH(CH_3)COOH$$

It soon became evident that the method was less satisfactory than the one finally adopted,[2] in which the a-hydroxy acid was obtained from methylethyl ketone.

It is the purpose of this paper to describe the synthesis of the diethyl ester of 3-hydroxybutane-2,2-dicarboxylic acid by the condensation of acetaldehyde with methylmalonic ester.

Discussion

The use of methyl iodide for the quantity production of methylmalonic ester is an expensive procedure. We have found methyl bromide to be a satisfactory methylating agent with both malonic ester and acetoacetic ester. From the standpoint of cost it possesses a distinct advantage over methyl iodide, and for one who must prepare his own reagent in quantity it possesses in addition the decided superiority of greater convenience, since the bromide can be prepared, purified and used in one operation. The yields obtained are, in the case of malonic ester, as satisfactory as any described in the literature and in the case of acetoacetic ester are somewhat better.

The condensation of acetaldehyde with methylmalonic ester was carried out by heating the reactants with acetic anhydride for fifty hours in sealed tubes at 104°. This reaction is undoubtedly similar to the one between acetaldehyde and malonic ester[3] in which ethylidene malonic

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[1] Du Pont Fellow in Chemistry, 1928–1929.

[2] Young, Dillon and Lucas, THIS JOURNAL, 51,2528 (1929).

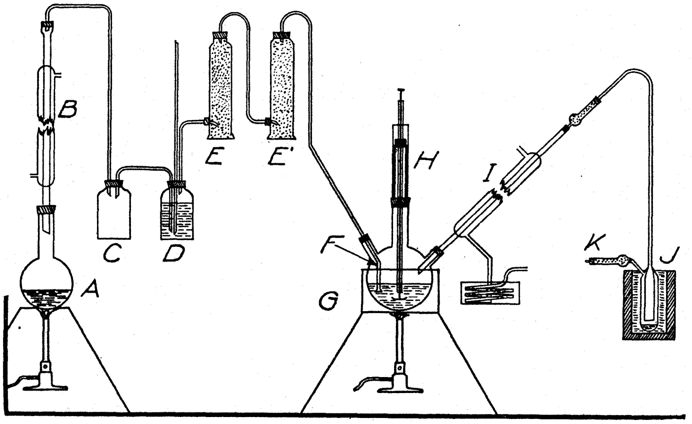
[3] Komnenos, Ann., 218,156 (1883).

ester is produced by the loss of water, involving the α-hydrogen atom. The condensation product from methylmalonic ester does not contain an a-hydrogen atom and thus an ethylidene derivative is not produced. However, a small amount of unsaturated ester results from the loss of water, involving a γ-hydrogen atom.

The condensation mixture was fractionally distilled at reduced pressure. Molecular weight determinations on the various higher fractions by the micro-method of Smith and Young[4] made it possible to tell which fractions contained the desired hydroxy ester. This procedure is a valuable aid in determining the approximate composition of various fractions.

Experimental

Methyl Bromide as a Methylating Agent.—The methyl bromide, generated in a 2-liter flask, *A* (see figure), from 215 g. (6.7 moles) of methanol, 266 g. (2.6 moles) of sodium bromide, 695 g. (7.0 moles) of 95% sulfuric acid and 230 g. of water according to the directions of Bygden,[5] was purified by passing it through concentrated sodium hydroxide, D, soda lime, *E*, calcium chloride, E', and led through the large tube *F*, flared at the lower end to a diameter of 22 mm., into the three-necked, 3-liter flask, *G*. This contained a solution of sodium malonic ester prepared from 350 cc. of absolute ethanol, 25 g. (1.1 moles) of metallic sodium and 160 g. (1.0 mole) of malonic ester (Eastman). The **flask** *G* was surrounded by a water-bath at 80–85° and the solution was agitated with a mechanical stirrer, H. **A reflux** cooler, **I**, condensed the alcohol



A, methyl bromide generating flask, 2-liter; B, reflux cooler; C, safety bottle; D, concentrated sodium hydroxide; E, soda lime tower; E', calcium chloride tower; *F*, flared inlet tube; G, flask, 3-liter, containing sodium malonic ester in ethanol; *H*, mechanical stirrer (mercury seal); **I**, reflux cooler; *J*, tube at −15°; K, calcium chloride tube.

Fig. 1.

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[4] Smith and Young, *J. Biol. Chem.*, 75,289 (1927).

[5] Bygden, J. *prakt.* Chem., 104, 285–288 (1922).

vapor, and any unreacted methyl bromide was condensed in the tube *J*, kept at −30° by an ice–hydrochloric acid mixture and provided with a calcium chloride tube, K. The generation of the methyl bromide was regulated by the rate of heating of the flask *A* and was made as fast as was consistent with effective purification. Soon after the gas flow was started sodium bromide precipitated in the reaction mixture and during an hour and one-half no trace of methyl bromide condensed in the tube J. Shortly after this a liquid began to collect in *J*. The reaction mixture was then tested with litmus and found to be neutral. The alcohol was distilled by heating the flask in an oil-bath at 125–130°, the least quantity of water was added for dissolving the salt, the resulting oil layer separated and the aqueous phase was extracted three times with 50 cc. of ether. The ether extracts and the crude ester were combined and dried overnight with anhydrous sodium sulfate. The ether was removed from the dried solution by heating over a water-bath at 50–80°, and the residue of crude methyl malonic ester was fractionally distilled through a 30-cm. bead column at reduced pressure, the main fraction boiling at 113.5–114° at 4648 mm. The yield was 80%. Since the boiling points of malonic, methylmalonic and dimethylmalonic esters lie within three and one-half degrees of each other,[6] the purity of the product obtained by the procedure outlined could not be told by its boiling range. Nevertheless, it was largely the desired methylmalonic ester, as shown by conversion to the free acid and decomposition of this to the monobasic acid. Now the melting point of 125.5–126.5° obtained for the dibasic acid does not distinguish between malonic and methylmalonic acids,[7] but the boiling point of the monobasic acid, 140–141°, indicated that the latter was largely propionic acid. The absence of acetic acid in this product, and therefore of malonic ester in the methylated ester, was likewise indicated by the successive values of 14.0 and 12.5 obtained for the Duclaux numbers.[8] These values were a trifle high for propionic acid, indicating the presence of a small quantity of isobutyric acid.

The methylmalonic ester prepared above had properties identical with the product obtained when methyl iodide was used, following the method of Conrad.[9] The melting points of the methylmalonic acids and the Duclaux numbers of the monobasic acids obtained by both methods were identical. It is thus evident that methyl iodide may be replaced by methyl bromide in a malonic ester synthesis.

Methyl bromide was likewise used in the synthesis of methylacetoacetic ester with satisfactory results. The product, obtained in 83% yields, was identical with that obtained by the use of methyl iodide.

Diethyl Ester of 3-Hydroxybutane-2,2-dicarboxylic Acid.—A mixture of 40 g. (0.23 mole) of methylmalonic ester, 47.0 g. (0.46 mole) of acetic anhydride and 21.0 g. (0.48 mole) of acetaldehyde (freshly prepared by the depolymerization of paraldehyde) was divided into portions of 35 cc. each, sealed in tubes and heated at 140° for fifty hours. The tubes were opened and the combined reaction mixture was fractionally distilled at reduced pressure. The fractions obtained are shown in Table I.

By running molecular weight determinations on several of the higher fractions by the camphor method of Smith and Young,[4] it was possible to identify the fractions containing the desired hydroxy ester, which has a molecular weight of 218. Two more fractionations of distillates 5, 6, 7 and 8 gave a fraction boiling at 94–98' at 2 mm. This material, after washing with sodium carbonate solution, distilled at 100–106° under 3–5 mm. pressure and weighed 17 g. The yield was 63%, based on the methylmalonic ester

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[6] Meyer and Bock, **Ann.**, **347**, 94 (1906).

[7] Salzer, *J. prakt. Chem.*, **61**, 166 (1900); ref. 6, p. 100.

[8] Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, 1923, p. 139.

[9] Conrad, **Ann.**, **204**, 134 (1889).

TABLE I

FRACTIONATION OF CONDENSATION PRODUCT FROM METHYLMALONIC ESTER AND ACETALDEHYDE

	Temp., °C.	Press., mm.	Weight, g.	Mol. wt.	Remarks
1	20–95	50	37	...	Acetic acid, acetic anhydride
2	95–112	50	18	...	Methylmalonic ester, mostly 110–112°
3	80–90	17–18	3	...	Mixtures
4	90–97	17–18	5.5	...	Mixtures
5	97–104	17–18	4.5	195	Probably the unsaturated ester[a]
6	100–110	8	3.5	200	Probably the unsaturated ester[a]
7	110–125	8	8	218	Desired product.
8	91–104	1–2	10	236	Desired product, but less pure
9	104–130	1–2	1	...	....
10	Residue	...	6.6	...	....

[a] Gave usual tests for unsaturation.

reacted. The results of molecular weight determinations by the camphor method on this purified product were 215 and 221 (theoretical, 218). The density, d^{21}_{4} was 1.0732.

Anal. Subs., 0.2180, 0.2101: H_2O, 0.1510, 0.1467; CO_2, 0.4405, 0.4247. Calcd. for $C_{10}H_{18}O_5$: H, 8.31; C, 55.0. Found: H, 7.76, 7.81; C, 55.1, 55.1.

Attempts to saponify the ester with alcoholic potassium hydroxide gave a reddish brown precipitate of high molecular weight. We were unsuccessful in obtaining a derivative with acid chlorides, the reaction yielding instead an unsaturated compound, probably the unsaturated ester. Apparently with acid chlorides water is eliminated very easily as might be expected from derivatives of β-hydroxy esters, although with acetic anhydride at 104°, a condition prevailing in the condensation reaction, dehydration was not an important factor, for the fraction of unsaturated ester did not exceed 10%. The presence of the hydroxyl group was demonstrated, since on addition of sodium hydrogen was evolved and a solid was formed. In order to establish completely the identity of the diethyl ester of 3-hydroxybutane-2,2-dicarboxylic acid, it was converted into the diamide.

Diamide of 3-Hydroxybutane-2,2-dicarboxylic Acid.—When 7.0 g. of the hydroxy ester was shaken with concentrated ammonium hydroxide the oil slowly went into solution during the course of eight days. From the aqueous solution evaporation yielded a white solid, readily soluble in water and sparingly soluble in absolute alcohol. Recrystallization from hot absolute alcohol gave 3 g. of pure white prisms melting at 209.5° (corr.) with decomposition. From 0.1042 g. there was obtained 16.40 cc. of nitrogen by the Dumas method, corresponding to 17.82%, whereas the theoretical value calculated from $C_6H_{12}O_3N_2$ is 17.48%.

The authors are indebted to Mr. R. T. Dillon for the analysis of the diamide.

Summary

Methyl bromide may satisfactorily replace methyl iodide in the preparation of the methyl derivatives of malonic ester and acetoacetic ester.

Acetaldehyde in the presence of acetic anhydride condenses with the ethyl ester of methylmalonic acid to produce the diethyl ester of 3-hydroxybutane-2,2-dicarboxylic acid.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

DERIVATIVES OF 2,5-DIBROMONITROBENZENE

BY L. CHAS. RAIFORD AND B. C. BREN

RECEIVED APRIL 8, 1929 PUBLISHED AUGUST 7, 1929

Of the dibromonitrobenzenes, the 2,5-isomeride[1] has been studied but little. Three derivatives were found on record, and of these only one was a reduction product, *viz.*, the aniline, which was prepared in the usual way.[2] The present report includes observations on the aniline and on products obtainable by reduction in alkaline mixtures.

Of the products theoretically possible by alkaline reduction the azoxy and azo compounds were obtained in small yields. Attempts to prepare the hydrazo compound and the isomeric benzidine by starting with the nitro compound were unsuccessful. When the azo compound was subjected to the action of stannous chloride and hydrochloric acid, as directed by Jacobson,[3] with the hope of converting it to the hydrazo compound and rearranging the latter to the benzidine, a yield of 42% of 2,5-dibromo-aniline was obtained and nothing else could be isolated from the mixture.

Following the directions of Knoevenagel,[4] 2,5-dibromo-aniline was diazotized with amyl nitrite and converted into a nearly colorless diazonium salt that decomposed explosively above 117°. Boiling this salt with water gave no phenol, but reduction of its alcoholic solution with stannous chloride and hydrochloric acid gave 2,5-dibromo-aniline and 59% of the ammonia required by the equation.[5] The diazonium salt readily reacts with

$$C_6H_3Br_2N_2X + 6(H) \longrightarrow C_6H_3Br_2NH_2 + NH_4X$$

the aniline, when the experiment is conducted by Noelting and Kopp's[6] method, to give a nearly quantitative yield of the diazoamino compound, which latter could not be rearranged to the aminoazo body. Reduction of this product with stannous chloride and hydrochloric acid gave 2,5-

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[1] Many derivatives of the 2,5-dichloro compound have been prepared by Noelting and Kopp [*Ber.*, 38, 3506 (1905)] and by Crowell and Raiford [THIS JOURNAL, 42, 145 (1920)].

[2] Meyer and Stuber [*Ann.*, 165, 180 (1873)] obtained the aniline by reduction of the nitro compound with tin and hydrochloric acid, but recorded no yield. Meldola and Andrews [*Proc. Chem. Soc.*, 11, 110 (1895)] could not reduce with zinc dust and acetic acid, and found that the alcoholic solution must be boiled with tin and hydrochloric acid to give satisfactory results.

[3] Jacobson, *Ann.*, 287, 147 (1895).

[4] Knoevenagel, *Ber.*, 23, 2995 (1890).

[5] Fischer [*Ann.*, 190, 78 (1878)] found that the diazonium salt from aniline is reduced by sodium sulfite to phenylhydrazine, while Meyer and Lecco [*Ber.*, 16, 2976 (1883)] obtained the same results with stannous chloride and hydrochloric acid.

[6] Noelting and Kopp, *Ber.*, 38, 3507 (1905).

dibromo-aniline and ammonia.' With β-naphthol the diazonium salt coupled to give an azo dye.

Derivatives of 2-Nitro-4-bromo-anisole.—This ether," obtained here from the dibromonitrobenzene by Blom's[9] method, was converted to the corresponding azoxy compound in four different experiments. The methyl alcoholic solution was reduced (1) with metallic sodium as directed by Starke;[10] (2) with sodium amalgam by Kanonnikow's[11] method; (3) by Brand's[12] electrolytic method and (4) by treatment with aqueous sodium hydroxide and zinc dust at 45° or below. The corresponding azo compound was obtained by (1) reduction of the azoxy derivative with sodium amalgam at 70°; (2) by reduction of the nitroanisole with sodium amalgam at 70°; (3) by electrolytic reduction of the nitro compound as directed by Elbs and Kopp,[13] and (4) by treatment of the alcoholic solution of the nitro compound with zinc dust and alkali, as recommended by Starke for reduction of o-nitro-anisole. Continued treatment with excess of zinc gave a small yield of what appeared to be the hydrazo compound.[14] This product was converted to the benzidine by the usual treatment with hydrochloric acid, while an attempt to benzoylate it caused rearrangement and the formation of the dibenzoylbenzidine.[15] The benzidine was further characterized by diazotization and coupling the product with β-naphthol to give an azo dye.

2-Nitro-4-bromophenetole obtained by Blom's method was converted into the azo compound by the various methods described above for the anisole. Attempts to reduce further with stannous chloride and hydrochloric acid did'not give the hydrazo compound and the expected diphenetidine, but 4-bromo-o-phenetidine. However, the hydrazo compound was obtained in small yield directly from the nitro compound, by the method used with the anisole. It was readily oxidized to the azo compound as explained above.

Experimental Part

The 2,5-dibromonitrobenzene used as starting material in this work was obtained by nitration of p-dibromobenzene, as outlined by Crowell and Raiford[16] for the chlorine compound. The derivatives were prepared by the standard methods indicated, the details of which will be omitted. The physical constants and analytical data for these products are shown in Tables IA and IB.

Summary

1. 2,5-Dibromo-aniline has been converted into a diazonium salt that did not give a phenol when boiled with water, but which coupled with β-

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[7] Fischer [*Ann.*, 190, 78 (1878)] found that the unsubstituted compound gave aniline and phenylhydrazine.

[8] First prepared by Staedel [*ibid.*, 217, 57 (1883)].

[9] Blom, *Helv. Chim. Acta*, 4, 1029 (1921).

[10] Starke, *J. prakt. Chem.*, [2] 59, 206 (1899).

[11] Kanonnikow, *Ber.*, 18 (Ref.) 611 (1885).

[12] Brand, *J. prakt. Chem.*, 67, 145 (1903).

[13] Elbs and Kopp, *Z. Elektrochem.*, 5, 108 (1898).

[14] The reactivity of the compound toward oxygen prevented the isolation of a pure product. When air was bubbled for 48 hours through a ligroin solution of this material at 50° it was converted into the azo compound.

[15] Stem, *Ber.*, 17, 379 (1884).

[16] Crowell and Raiford, THIS JOURNAL, 42, 147 (1920).

TABLE IA

DERIVATIVES OF 2,5-DIBROMONITROBENZENE

	Compound	Solvent	Crystal form	Yield, %
1	Tetrabromoazoxybenzene	Alcohol	....	15
2	Tetrabromoazobenzene	Alcohol	Red needles	13
3	Tetrabromodiazoaminobenzene	Alcohol	Yellow needles	Nearly quant.
4	Dibromophenyldiazonium chloride	Alc. and ether	Colorless granules	....
5	Dye	Alc and ligroin	Red needles	....
6	5,5′-Dibromoazoxy-*o*-anisole	Alcohol	Straw-colored needles	60
7	5,5′-Dibromoazo-*o*-anisole	Pyridine	Red needles	81
8	5.5'-Dibromohydrazo-o-anisole	Ligroin	Nearly colorless needles	Very small
9	6,6′-Dibromodianisidine	Alcohol	Fawn-colored plates	60
10	Dibenzoyldianisidine	Ligroin	Granules	Nearly quant.
11	Dye	....	Amorphous red powder	....
12	5,5-Dibromohydrazo-o-phenetole	Ligroin	Colorless needles	14

TABLE IB

DERIVATIVES OF 2,5-DIBROMONITROBENZENE

	Formula	M. p., °C.	Subs., g.	Ag hal., g.	Halogen, % Calcd.	Halogen, % Found
1	$C_{12}H_6ON_2Br_4$	217	0.1027	0.1500	62.25	62.15
2	$C_{12}H_6N_2Br_4$	247	.0973	.1466	64.25	64.12
3	$C_{12}H_7N_3Br_4$	185[a]	.1028	.1463	62.38	61.97
4	$C_6H_3N_2ClBr_2$	...	.1103	.1194	65.49	65.32
5	$C_{16}H_{10}ON_2Br_2$	...	.1562	.1444	39.37	39.34
6	$C_{14}H_{12}O_3N_2Br_2$	121	.1014	.0914	38.46	38.37
7	$C_{14}H_{12}O_2N_2Br_2$	238	.1034	.0970	40.00	39.91
8	$C_{14}H_{14}O_2N_2Br_2$	120–121[b]	...	....	...	...
9	$C_{14}H_{14}O_2N_2Br_2$	168	.1089	.1017	39.80	39.74
10	$C_{28}H_{22}O_4N_2Br_2$	274	,1997	.1218	26.22	25.95
11	$C_{34}H_{24}O_4N_4Br_2$	...	.2972	.1561	22.47	22.35
12	$C_{16}H_{18}O_2N_2Br_2$	171-172	.1199	.1044	37.20	37.05

[a] A product which appeared to have this composition was reported by Meldola and Andrews, Proc. Chem. *Soc.*, 11, 110 (1895). to melt at 234–235°.

[b] Analytical data were not satisfactory.

naphthol to give an azo dye. It coupled with aniline to give a diazo-amino compound, but the latter could not be rearranged into the isomeric aminoazo compound. Treatment of the diazonium salt with stannous chloride and hydrochloric acid did not give the expected hydrazine, but regenerated the amine and split off ammonia.

2. Of the reduction products expected in alkaline mixtures, only the azoxy and the azo compounds were obtained.

3. The monobromo-anisole and phenetole prepared from the dibromonitrobenzene gave, in addition, the respective hydrazo compounds.

IOWA CITY, IOWA

BETA-PHENYLISOBUTYLMETHYL KETONE AND ITS DERIVATIVES. THE SYNTHESIS OF ALPHA- AND OF BETA-PHENYLISOVALERIANIC ACIDS

BY ALFRED HOFFMAN

RECEIVED APRIL 12, 1929 PUBLISHED AUGUST 7, 1929

When mesityl oxide is added to benzene in the presence of anhydrous aluminum chloride, condensation takes place with the formation of a ketone $C_{12}H_{16}O$. It is likely that the hydrogen chloride addition product of mesityl oxide is formed first and then reacts with the aluminum chloride setting free hydrogen chloride. Thus a trace of hydrogen chloride catalyzes the reaction and an evolution of the free gas takes place only at the very end.

The presence of the carbonyl group in the new substance is shown by the formation of the oxime and the semicarbazone. If the latter, which is formed quantitatively, is fractionally crystallized, all fractions have the same melting point, showing that the ketone is a single substance and not a mixture of isomers.

As a methyl ketone it is easily oxidized by sodium hypobromite solution with the formation of a phenylisovalerianic acid which is identical with the one prepared by Eijkman[1] by the action of benzene on β,β-dimethylacrylic acid in the presence of aluminum chloride and characterized by a nitro derivative melting at 175°. In order to decide between the alpha and the beta forms of the acid, Eijkman treated his substance with benzaldehyde under the most varied conditions. As he failed to obtain any indication of a condensation, he inferred that there was no methylene group adjacent to the carboxyl group and that therefore his acid was the alpha form. This is not what might be expected in the present case. The chlorine of the addition product of mesityl oxide and hydrogen chloride has for good reasons been considered attached to the tertiary carbon atom, so that after replacement with phenyl and oxidation, β-phenylisovalerianic acid should be obtained. In order to decide the question, both alpha and beta acids were prepared by the malonic ester method. The results, as shown in the experimental part, give conclusive proof that the acid obtained from the ketone, and therefore also Eijkman's acid, is the beta form and that the reactions were as follows

$$(CH_3)_2C{=}CHCOCH_3 \longrightarrow (CH_3)_2CClCH_2COCH_3 \longrightarrow (CH_3)_2C(C_6H_5)CH_2COCH_3 \longrightarrow (CH_3)_2C(C_6H_5)CH_2COOH$$

β-Phenyl*iso*butyl methyl ketone does not react with sodium bisulfite. With a mixture of nitric and sulfuric acids it gives a nitro compound, which is soluble in sodium carbonate solution with a blood-red color. It is likely that this compound, which was not isolated in a pure state, contains a nitro group attached to an aliphatic carbon atom. Treated with

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[1] Eijkman, *Chem. Centr.*, **II**, 1100 (1908).

an excess of bromine in acetic acid, the ketone gives a crystalline tetrabromo derivative.

Of interest is the action of the ketone on heating with anhydrous zinc chloride. A mixture of hydrocarbons is obtained from which it is possible to isolate in fairly good yield a well-crystallizing substance melting at 130.5–131°. According to boiling point, molecular weight determination and analysis its formula is $C_{24}H_{28}$. It is therefore formed from two molecules of water. The hydrocarbon does not react with bromine in chloroform solution, even on heating or with the addition of iron powder or iodine. Boiled with concentrated nitric acid it gives a trinitro derivative, which is not soluble in sodium carbonate solution. Toward oxidizing agents the hydrocarbon is very resistant. Thus boiling with dilute nitric acid is without effect. Chromic acid in glacial acetic acid solution does not act in the cold; on boiling the solution slowly turns green. Most of the hydrocarbon remains intact; the rest seems to be completely oxidized, as no products such as benzoic acid or ketones could be isolated. Permanganate in moist acetone solution is not decolorized in the cold.

Boiling with aqueous permanganate for 142 hours gave but a small amount of manganese dioxide. The hydrocarbon was likewise unaffected by grinding with manganese dioxide and 50% sulfuric acid at 50°. According to these results about all that can be said as to the constitution of the hydrocarbon is that it is a very stable, saturated substance, probably of a cyclic nature.

The ketone may be reduced in the usual way with sodium and alcohol to form the corresponding alcohol, β-phenyl*iso*butylmethylcarbinol.

On treatment with zinc chloride, this alcohol loses a molecule of water, giving the hydrocarbon $C_{12}H_{16}$. The latter is unsaturated and easily oxidized in contact with air. Attempts to purify such material by distillation over sodium resulted in the loss of most of it by polymerization. It probably has the structure $(CH_3)_2C(C_6H_5)CH{=}CHCH_3$. Attempts to prove this by means of the oxidation products with chromic acid were not successful. A complicated mixture of ketones was obtained which was separated into fractions; these were converted into semicarbazones and recrystallized. Acetophenone was identified by mixed melting point; phenylacetone and propiophenone were absent. A special search was made for α-phenyl*iso*butyraldehyde in the fraction boiling around 110° (14 mm.). This fraction, however, did not reduce ammoniacal silver solution, nor could a high-melting semicarbazone be obtained.

Experimental Part

Preparation of β-Phenyl*iso*butyl Methyl Ketone.—Ninety grams of anhydrous aluminum chloride in granular form together with 200 cc of benzene is placed in a 500-cc. wide-mouthed Erlenmeyer flask. The latter is provided with a short vent-tube and a stirrer and cooled with water. Fifty grams of mesityl oxide is dropped in during an hour with thorough stirring, which is then continued for three hours longer. The mixture is poured on ice and the water separated. The oil is washed with water, filtered, poured into sodium carbonate solution and steam distilled to remove the excess benzene. The ketone itself is but slightly volatile with steam. After cooling, the oil is separated, dried over calcium chloride and distilled under diminished pressure; yield, **72** g.; calcd., **89** g. The product boils at 124° **(14 mm.)** and is pure enough for preparative purposes. It contains, however, a trace of halogen and discolors after standing for some time. In order to purify it, the semicarbazone is prepared, recrystallized and steam distilled with a large excess of phthalic anhydride. The ketone thus obtained is a water-white, highly refractive liquid which remains colorless indefinitely. The odor is somewhat like that of camphor, with a suggestion of roses; b. p. **134" (22** mm.); 252° corr. **(760 mm.)**; sp. gr. 25°/25°, **0.972.**

Anal. Calcd. for $C_{12}H_{16}O$: **C, 81.8; H, 9.09.** Found: C, **81.5;** H, **9.00.**

Preparation of the Semicarbarone.—Twenty-five grams of ketone was added to a concentrated aqueous solution of **17** g. of semicarbazide hydrochloride and **22** g. of crystallized sodium acetate with the addition of enough methyl alcohol to render the mixture homogeneous. After standing for twenty-four hours the product was recrystallized from methyl alcohol; yield, **31** g.; m. p., **163–164".**

Anal. Calcd. for $C_{13}H_{19}ON_3$: N, **18.03.** Found: N, **18.33.**

Preparation of the Oxime.—Ten and seven-tenths grams of ketone was treated with an aqueous solution of **4.5 g.** of hydroxylamine hydrochloride, **5.4 g.** of sodium bicarbonate and enough methyl alcohol to render it homogeneous. After standing for several hours at 50°, the product was poured into water, extracted with ether and distilled under diminished pressure; yield, **9.3** g.; b. p. 181° **(27 mm.)**; m. p. 52–54° (not recrystallized).

Anal. Calcd. for $C_{12}H_{17}ON$: N, **7.33.** Found: **N,** ***7.7.***

Preparation of the Tetrabromo Ketone.—The ketone reacts with bromine with explosive violence and therefore a diluent is necessary; **8.8** g. of ketone in **20** cc. of glacial acetic acid is gradually treated with **35** g. of bromine. After standing for a day, water is added, the red oil taken up with ether and washed with sodium bisulfite solution to remove excess bromine. The ether is evaporated and the residue recrystallized from methyl alcohol; it gives a crystalline, white powder; m. p. 96–98°.

And. Calcd. for $C_{12}H_{12}OBr_4$: Br, **65.0.** Found: Br, **64.9.**

Preparation of the Hydrocarbon, $C_{24}H_{28}$.—Sixteen and seven-tenths grams of ketone and **12** g. of anhydrous zinc chloride were heated in a small Erlenmeyer flask on a gauze over a free flame. The zinc chloride slowly dissolved and the mixture turned a vivid carmine. At about 180° a lively reaction took place and the liquid divided into two layers. On cooling, both layers solidified. The upper, white crystalline layer was dissolved in petroleum ether and distilled under diminished pressure. The use of an Anschiitz flask is advisable for this as the distillate has a tendency to solidify and clog up the side-neck. The fraction boiling from 150–230° **(18** mm.) **(8.6** g.) was pressed out between filter paper and recrystallized from petroleum ether; b. p. **195" (18** mm.); **m.** p. 130.5–131° corr. The material crystallized well in flat, white needles or plates.

Anal. Calcd. for $C_{24}H_{28}$: C, **91.1;** H, 8.9. Found: **C, 90.8;** H, **8.8.** *Mol. wt.* 0.021 **g.** of subs. in **0.132** g. of camphor gave 20° depression of melting point. Calcd. for $C_{24}H_{28}$: mol. wt., **316. Found: 318.**

Preparation of Trinitrohydrocarbon.—Two grams of hydrocarbon was refluxed with **30 cc.** of nitric acid **(1.42)** for nine hours. The oil finally dissolved without noticeable reaction but separated again on cooling. It was washed with water and recrystallized from much methyl alcohol; yield, **0.3** g. as fine white needles; m. p. 180–184°.

Anal. Calcd. for $C_{24}H_{25}(NO_2)_3$: N, 9.3. Found: N, 9.03.

Reduction of Ketone.—Ten grams of ketone was refluxed with 100 cc. of absolute alcohol in a one-liter flask and 20 g. of sodium was added rapidly through the condenser. After the reaction had quieted, 50 cc. more alcohol was added to dissolve the excess sodium. Then 68 cc. of water was added and the ethyl alcohol distilled off in an oil-bath. Water was added to the residue, the carbinol extracted with ether and distilled under diminished pressure; yield, 9.2 g.; b. p. 132–133° (17 mm.), sp. *gr.* 25°/25°, 0.960. It has little odor.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.89; H, 10.1. Found: C, 80.32; H, 9.9.

Dehydration of the **Carbinol.**—Seventeen and seven-tenths grams of the alcohol was heated with 14.5 g. of anhydrous zinc chloride over a free flame for one and one-half hours. After a slight reaction the mixture separated into two layers. After cooling, the upper layer was poured off and distilled; yield, 14.2 g.; b. p. 96–98° (17 mm.); sp. gr. 25°/25°, 0.889.

Anal. Calcd. for $C_{12}H_{16}$: C, 90.0; H, 10.0. Found: C, 88.1; H, 9.73.

The product was evidently not quite pure; it reacted instantly with bromine in chloroform. On oxidation with chromic acid in acetic acid solution, a complicated mixture was obtained boiling from 90° (18 mm.) to 150° (24 mm.). On recrystallizing the semicarbazones of the various fractions the only one identified was a small fraction of m. p. 186–189°. Mixed with acetophenone semicarbazone it melted at 187–189°.

Oxidation of the Ketone to **β-Phenylisovalerianic** Acid.—Seventeen and six-tenths grams of ketone was shaken with sodium hypobromite solution prepared from 24 g. of sodium hydroxide, 48 g. of bromine and 100 g. of ice and water. The mixture became warm after about five hours and at the end of 20 hours the reaction was complete. After separating the bromoform and filtering, the aqueous solution was acidified with dilute sulfuric acid with the addition of a little sodium bisulfite. An oil separated which solidified on standing. It was pressed out between filter paper to remove oily impurities and recrystallized from petroleum ether; yield, 11.2 g.; m. p., 58–58.5°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.86. Found: C, 73.9; H, 7.9.

The nitro derivative, prepared by heating with 75% nitric acid, melts at 169–172°.

The methyl ester boils 120° (11 mm.); 123° (12 mm.).

The anilide was prepared as follows for the purpose of further comparison with the synthetic α- and β-acids: 1.5 g. of acid and 2.3 g. of aniline were heated for nine hours in a small distilling flask in a graphite bath so that water and aniline slowly distilled off. The product was dissolved in ether, shaking out with dilute sulfuric acid and with sodium carbonate solution, the ether removed and the residue recrystallized from 60% methyl alcohol with the use of bone black; m. p., 122–123°.

Anal. Calcd. for $C_{17}H_{19}ON$: C, 80.6; H, 7.5. Found: C, 80.5; H, 7.2.

α-Phenylisovalerianic Acid.—The ethyl ester of phenylacetic acid was condensed with ethyl oxalate by means of alcohol-free sodium ethylate to form phenyloxalacetic ester. This, on heating, lost carbon monoxide, giving phenylmalonic ester. This method[2] is not very satisfactory, so it is welcome that a new method has recently appeared.[3] As found by Nelson and Cretcher in a similar case, the alkylation of phenylmalonic ester does not work well, much phenylacetic ester being formed. Eighteen and nine-tenths grams of phenylmalonic ester was added to a solution of 1.85 g. of sodium in 35 cc. of absolute alcohol and 25 g. of *iso*propyl iodide run in.

$$NaC(C_6H_5)(COOC_2H_5)_2 + (CH_3)_2CHI \longrightarrow (CH_3)_2CHC(C_6H_5)(COOC_2H_5)_2 \longrightarrow (CH_3)_2CHCH(C_6H_5)COOH$$

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[2] W. Wislicenus, *Ber.*, **27**, 1093 (1894).

[3] W. I,. Nelson and I,. H. Cretcher, THIS JOURNAL, 50, 2758 (1928).

The solution remained clear until heated and then slowly became cloudy. After boiling for fourteen hours it had become neutral. The alcohol was distilled off, water added, the product extracted with ether and distilled; yield, 12.3 g.; b. p., 165–190° (31 mm.). According to analysis it was a mixture of about one part of phenylacetic ester with three parts of *iso*propylphenylmalonic ester. Boiled with a solution of 16 g. of potassium hydroxide in 68 cc. of water it dissolved completely in about ninety hours. Alcoholic potassium hydroxide or more concentrated aqueous solutions did not work as well. The acid was liberated by adding dilute sulfuric acid and extracting with ether. Yield: 5.4 g.; b. p., 165–168° (25 mm.). As little gas was given off during the distillation, one molecule of carbon dioxide had been split off during the long boiling. Pickard and Yates[4] found the same in the case of phenylallylmalonic ester. In order to remove the phenylacetic acid present, the acid was boiled with water and barium carbonate, the aqueous solution of the very soluble barium salts filtered and treated with silver nitrate solution. The granular precipitate of silver salts was thoroughly washed with water to remove the fairly soluble silver phenylacetate. The salt of α-phenylisovalerianic acid is only slightly soluble.

Anal. Calcd. for $C_{11}H_{13}O_2Ag$: Ag, 37.9. Pound: Ag, 38.1.

To obtain the free acid, 9.7 g. of silver salt was shaken with ether and 5 g. of nitric acid in 100 cc. of water; yield, 5.1 g.; b. p., 159–160° (14 mm.); m. p., 60°. The odor is similar to that of phenylacetic acid but more disagreeable and clinging. The acid prepared from the ketone as well as the synthetic β-acid does not have a pronounced odor.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.86. Found: C, 74 1; H, 7 89.

It was not found possible to obtain a solid nitro compound by heating with 75% nitric acid.

The anilide melted at 132–133°.

Anal. Calcd. for $C_{17}H_{19}ON$: C, 80.6; H, 7.5; N, 5.53. Found: C, 81.1; H, 7.7; N, 5.8.

$$C_6H_5C(CH_3)_2Cl + NaCH(COOC_2H_5)_2 \rightarrow C_6H_5C(CH_3)_2CH(COOC_2H_5)_2 \longrightarrow C_6H_5C(CH_3)_2CH_2COOH$$

β-Phenylisovalerianic Acid.—Dimethylphenylcarbinol was prepared by the action of methylmagnesium iodide on acetophenone and the hydroxyl substituted with chlorine by saturating with dry hydrogen chloride at 0°.[5] These reactions worked smoothly. The crude chloride prepared in this manner from 18.6 g. of the carbinol was poured on ice, extracted with ether, washed with sodium bicarbonate solution and dried carefully with anhydrous sodium sulfate. The ethereal solution was then added to a solution of 3.2 g. of sodium and 22 g. of ethyl malonate in 35 g. of absolute alcohol. The clear mixture gradually became cloudy and after twelve hours contained considerable precipitate. It was still slightly alkaline but became neutral after the ether and part of the alcohol had been distilled off. Water was added and the product extracted with ether. On distilling almost all came over up to 119°, 17 mm. Evidently the chief reaction is

$$C_6H_5CCl(CH_3)_2 + NaCH(COOC_2H_5)_2 \longrightarrow C_6H_5C(CH_3){=}CH_2 + H_2C(COOC_2H_5)_2 + NaCl$$

A small residue boiled at 150–180° (13 mm.); yield, 4.3 g. Without further purification it was boiled with 7.5 g. of potassium hydroxide in 14 cc, of water. The oil dissolved in two hours, with the exception of a few drops having a strong odor; these were distilled off with steam. The liquid was acidified with sulfuric acid and extracted twice with ether. After removing the ether, the residue was heated to 200° in an oil-

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[4] Pickard and Yates, J. *Chem. Soc.*, 95, 1015 (1909).

[5] Klages, Ber., 35,2638 (1902).

bath and, after the foaming and evolution of gas had ceased, was distilled; yield, 1.58 g.; b. p., 163° (8 mm.), 167° (10 mm.); m. p., 57.5–58.5°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.86. Found: C, 73.9; H, 7.9.

Heated with 75% nitric acid a nitro compound was formed: m. p. 166–168" (not recrystallized). The anilide melted at 121–123°.

The following table gives the melting points and the mixed melting points of the various derivatives and shows the identity of the acid from the ketone with the synthetic beta acid.

TABLE I

PHYSICAL CONSTANTS

		Acid, m. p., °C.	Nitro deriv., m. p., °C.	Anilide, m. p., °C.
1	Acid from ketone	58–58.5	169–172	122–123
2	α-Acid	60	.....	132–133
3	β-Acid	57.5–58.5	166–168	121–123
	1 + 2	35–40	.....	110–119
	1 + 3	57.5–58.5	166–170	121–123

Summary

Mesityl oxide has been found to react with benzene in the presence of anhydrous aluminum chloride to give β-phenyl*iso*butyl methyl ketone. Of the latter a semicarbazone, an oxime, a nitro and a tetrabromo derivative have been prepared. Treated with anhydrous zinc chloride the ketone yields a saturated, stable, crystalline hydrocarbon, $C_{24}H_{28}$, which gives a trinitro derivative. The ketone was reduced to the carbinol, from which an unsaturated hydrocarbon, $C_{12}H_{16}$, is produced by the action of zinc chloride. On oxidation with sodium hypobromite solution, the ketone gives a phenylisovalerianic acid which is identical with one described by Eijkman as the a-phenyl acid. By the synthesis of both the a- and the β-phenylisovalerianic acids by the malonic ester method, it is shown that the acid from the ketone is the β-acid. The true a-acid has not before been prepared.

KEW GARDENS, NEW YORK

[CONTRIBUTION NO. 10 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

STUDIES ON POLYMERIZATION AND RING FORMATION. I. AN INTRODUCTION TO THE GENERAL THEORY OF CONDENSATION POLYMERS

BY WALLACE H. CAROTHERS

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Polymerization frequently leads to substances of very high molecular weights, and the problem of the structure of high polymers is attracting a great deal of attention, especially because such important materials as rubber, cellulose, proteins and resins either are high polymers or have certain properties which are common to high polymers.

The conditions which Berzelius[1] was concerned to recognize by the term polymer were the presence of the same atoms in the same proportions in compounds having different molecular weights. These conditions are satisfied by the members of a great many thousand pairs of compounds which are not now regarded as polymers. Thus, of the compounds paracetaldehyde, butyric acids and hydroxycaproic acids, only the first would now be considered a polymer of acetaldehyde, although there is nothing in the conditions of the Berzelius definition to exclude the others. Hence, whatever the term polymer may mean now, it does not mean precisely what Berzelius intended, and the conditions which he set up are not sufficient to define it. In current attempts to define this term[2] it is still stated that a polymer and its monomer must have the same atoms in the same proportions. But this condition is not satisfied by the polyoxymethylenes (see Table I) which are universally considered to be polymers of formaldehyde. It seems desirable, therefore, to attempt to formulate a definition which will be in so far as possible in accordance with both the current usage and the essential facts.

The structures of a good many polymers, including some of very high molecular weights, are known either completely or in part and an examination of their formulas shows some interesting relationships (see Table I). They are characterized by a recurring structural unit, so that if this is represented by $-R-$, the structure of these polymers may be represented in part by the general formula $-R-R-R-R-R-R-R-R-$, etc., or $(-R-)_n$. In this formula n may be small as in paracetaldehyde $(n = 3)$, or it may be very large as in the polyoxymethylenes. The end valences may be united as they are in paracetaldehyde to form a ring, or they

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[1] Berzelius, *Jahresbericht*, 12, 63 *(1833)*.

[2] Hess, "Chemie der Zellulose," Leipzig, 1928, p. 577; Meerwein, Houben-Weyl, "Die Methoden der organischen Chemie," Leipzig, 1923, Zweite Auflage, dritter Band, p. 1013; Staudinger, Ber., 58, 1074 (1920).

may be saturated by univalent groups such as H— and —OH to form an open chain of the type $\text{H}(\text{—R—})_n\text{OH}$ as they are in α-polyoxymethylene. It seems probable that cellulose and silk fibroin are of this type, and in any event it may be observed that no high polymer is certainly known to be cyclic.[3] There are polymers which do not conform to the type $(\text{—R—})_n$ but those which do will be called linear whether the chain is open or closed; and the subsequent discussion is concerned only with these.

The structural units —R— are bivalent radicals which, in general, are not capable of independent existence. The presence of a recurring structural unit is, of course, characteristic of most organic compounds (e. g., $\text{—CH}_2\text{—}$ in aliphatic compounds), but in the case of polymers there exists a molecule, the monomer, corresponding to the structural unit, and from which the polymer may be formed or to which it may be degraded.

Examination of the formulas of Table I will show that two types of polymers may be distinguished. In the first type, which includes paracetaldehyde, rubber, polystyrene and polyoxymethylenes, the molecular formula of the structural unit is identical with that of the monomer, *i. e.*, the formula of the structural unit, —R—, is isomeric with that of the monomer. In the second type, which includes the polyethylene glycols, cellulose and silk fibroin, the molecular formula of the structural unit differs from that of the monomer by H_2O, *i. e.*, the monomer is H—R—OH. The transformation of polymers of the first type into their monomers is brought about simply by heating, and the reverse transformation (polymerization) occurs spontaneously or by the action of catalysts. In the second type, degradation to the monomer occurs by hydrolysis, and if the reverse process were to take place it would require the elimination of water among many molecules. This would be polyintermolecular condensation.[4]

These two classes will be distinguished as (1) addition or A polymers. The molecular formula of the monomer is identical with that of the structural unit. The monomer can be obtained from the polymer by thermolysis or the polymer can be synthesized from the monomer by self-addition. (2) Condensation or C polymers: the molecular formula of the monomer differs from that of the structural unit. The monomer can be obtained from the polymer by hydrolysis or its equivalent or the polymer can be synthesized from the monomer by polyintermolecular condensation. Polymerization then is the chemical union of many similar molecules

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[3] However, Staudinger, in his latest papers, favors the view that polystyrene and rubber are very large rings, *Ber.*, 62,241 (1929).

[4] The term condensation is used here to name any reaction which occurs with the formation of a new bond between atoms not already joined and which proceeds with the elimination of elements (H_2, N_2, etc.) or of simple compounds (H_2O, C_2H_5OH, NH_3, NaBr, etc.). Examples are the Wurtz reaction, Friedel–Crafts reaction, esterification, etc.

either (A) without or (C) with the elimination of simpler molecules (H_2O, HCl, $NaCl$, NH_3, etc.).[5]

Assuming that polyintermolecular condensation exists, the above examples and definitions and their implications provide ample reason for referring to this process as a type of polymerization. These examples, of course, do not provide any proof that this process as distinct from and independent of A polymerization does exist. This proof will appear incidentally in the following discussion, which is concerned with the general principles involved in the formation of condensation polymers.

Polyfunctional Compounds.—Polyintermolecular condensation requires as starting materials compounds in which at least two functional groups are present in the same molecule (*e. g.*, hydroxy acids, HORCOOH, might lead to poly-esters, HORCOORCOORCOORCOORCOORCO—, etc.; amino acids, to poly-amides, $NH_2RCONHCONHRCONHRCONHRCONHRCO$—, etc.).

Among compounds having more than one functional group, those of the type x—R—y may be called bifunctional, $R''x_3$, trifunctional, etc. In these formulas R stands for a bivalent radical (R" for a trivalent radical) and x and y for functional groups capable of reacting with each other in a known fashion to form the new functional group z. Thus x—R—y ⟶ —R—z—, where —R—z— evidently represents a structural unit which will appear in the product and which may be present 1, 2, 3, . . . *n* times. Reactions of this type will be called bifunctional regardless of the number of molecules involved. Reactions of the type x—R—x + y—R′—y ⟶ —z—R—z—R′— may be called bi-bifunctional. All such reactions may, at least by hypothesis, pass through the stage x—R—x—R'—y which is equivalent to x—R—y, and for purposes of discussion they may therefore be classed as simple bifunctional reactions. Reactions of the type $R'x_3 + Ry_2 \longrightarrow$ *product* will be called tri-bifunctional. Similarly there may be tetra-bifunctional, tri-trifunctional reactions, etc., and all these may be classed together as polyfunctional reactions. The present discussion is concerned only with bifunctional reactions.

Bifunctional Reactions.—These always present two possibilities: they may be intramolecular or intermolecular. If intramolecular they can

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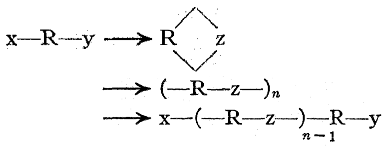
[5] It would not be difficult to suggest examples in which a single polymer might belong to either or to both of these classes depending upon the method by which it was synthesized. So far as cellulose is concerned there is little to justify its classification as a C rather than as an **A** polymer other than the criteria which are set forth in the above definitions, and these may at present appear somewhat arbitrary. Thus even if cellulose were synthesized by the dehydration of glucose, this might occur by the formation of a glucosan which subsequently polymerized by self-addition. It may be observed, however, that of the two trimethylglucosans which might conceivably polymerize in this way to form trimethylcellulose, one is known and does not polymerize, and the other is probably incapable of existence on stereochemical grounds. See Freudenberg and Braun, ***Ann.***, 460,288 (1928).

lead only to the simple monomeric ring I. If intermolecular they may lead either to a polymeric ring II or to a polymeric chain III.



I

II

III

These obviously represent three possibly competing reactions.

The question now arises, what factors will determine which of these possible courses a bifunctional reaction will take? It is obvious, for example, that in general dilution would favor intra- over intermolecular reaction.[6] Temperature and catalysts might favor either one or the other. It appears, however, that structural and stereochemical factors will usually be more important than any others. That is, though it may be possible in some bifunctional reactions to control the choice between intra- and intermolecular reaction by suitable adjustment of experimental conditions, this choice will, in general, be almost completely determined by the nature of the reacting molecules.

The effects of these factors may be stated as follows. (1) If the product of intramolecular reaction would be a ring which, on stereochemical grounds, is incapable of existence, reaction will be intermolecular. This is apparently the case with p-$NH_2C_6H_4CH_2CH_2Cl$, which reacts with itself intermolecularly,[7] and not as had previously been supposed[8] with the formation of the so-called dihydro-p-indole? The utility of this very obvious principle is somewhat diminished by the fact that, in the present state of stereochemical knowledge, it is sometimes impossible to predict whether a given ring system will be capable of existence or not.

(2) Bifunctional reactions which can lead to the formation of 5- or 6-rings almost invariably proceed intramolecularly. This well-established fact is responsible for the existence of the majority of the very large number of 5- and Brings which is known.

(3) Bifunctional reactions which, if intramolecular, could lead only to larger-than-6-rings, generally proceed intermolecularly and lead to polymeric products. If this rule were free from any exceptions, it would necessarily follow that the polymeric products would always be of the open-chain type, III.

Although a great many bifunctional reactions have been studied in the hope of forming large rings, our information as to the precise nature of the

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[6] *Cf.* Ruggli, *Ann.*, 392, 92 (1912), where the recognition of this principle made possible the synthesis of large rings containing an acetylenic linkage.

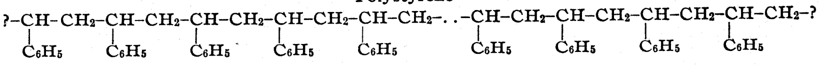
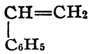
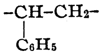
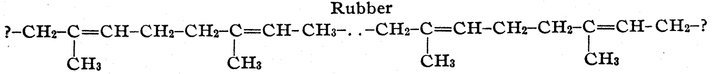
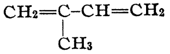
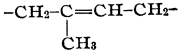
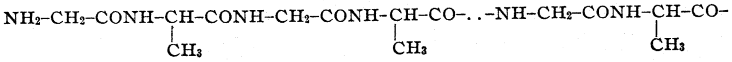
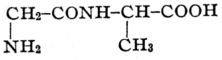
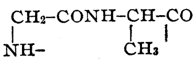
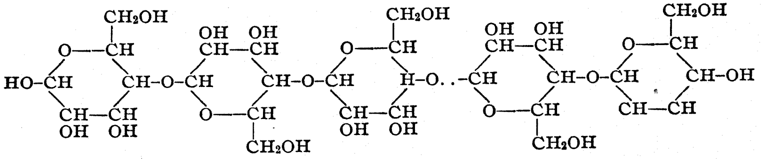
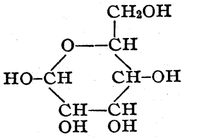
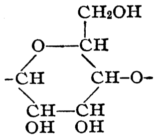
[7] Ferber, ***Ber.***, 62, 183 (1929).

[8] V. Braun and Gawrilow, *ibid.*, 45, 1274 (1912).

[9] For some other examples, see Titley, J. Chem. *Soc.*, 2571 (1928).

TABLE I

POLYMERS

Polymer		Monomer	Mer or structural unit
Polystyrene  $?\mathrm{-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2-..-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2-}?$	$\overset{\text{heat}}{\rightleftarrows}$	Styrene  $\mathrm{\underset{C_6H_5}{CH}=CH_2}$	 $\mathrm{-\underset{C_6H_5}{CH}-CH_2-}$
Rubber  $?\mathrm{-CH_2-\underset{CH_3}{C}=CH-CH_2-CH_2-\underset{CH_3}{C}=CH-CH_3-..-CH_2-\underset{CH_3}{C}=CH-CH_2-CH_2-\underset{CH_3}{C}=CH-CH_2-}?$	$\overset{\text{heat}}{\rightleftarrows}$	Isoprene  $\mathrm{CH_2=\underset{CH_3}{C}-CH=CH_2}$	 $\mathrm{-CH_2-\underset{CH_3}{C}=CH-CH_2-}$
α-Polyoxymethylene $\mathrm{HO-CH_2-O-CH_2-O-CH_2-O-CH_2-O-..-CH_2-O-CH_2-O-CH_2-O-CH_2-OH}$	$\overset{\text{heat}}{\rightleftarrows}$	Formaldehyde $\mathrm{H_2C=O}$	$\mathrm{-CH_2-O-}$
β-Polyoxymethylene $\mathrm{HSO_3-O-CH_2-O-CH_2-O-CH_2-O-CH_2-O-..-CH_2-O-CH_2-O-CH_2-O-H}$	$\overset{\text{heat}}{\rightleftarrows}$	$\mathrm{H_2C=O}$	$\mathrm{-CH_2-O-}$
Polyethylene glycols $\mathrm{HO-CH_2-CH_2-O-CH_2-CH_2-O-..-CH_2-CH_2-OH}$	$\xrightarrow{\text{HOH}}$	Ethylene glycol $\mathrm{HO-CH_2-CH_2-OH}$	$\mathrm{-CH_2-CH_2-O-}$
Silk fibroin  $\mathrm{NH_2-CH_2-CONH-\underset{CH_3}{CH}-CONH-CH_2-CONH-\underset{CH_3}{CH}-CO-..-NH-CH_2-CONH-\underset{CH_3}{CH}-CO-}$	$\xrightarrow{\text{HOH}}$	Glycyl alanine  $\mathrm{\underset{NH_2}{CH_2}-CONH-\underset{CH_3}{CH}-COOH}$	 $\mathrm{\underset{NH-}{CH_2}-CONH-\underset{CH_3}{CH}-\underset{\mid}{CO}}$
Cellulose 	$\xrightarrow{\text{HOH}}$	Glucose 	

The above formulas for the polyoxymethylenes, polystyrenes and rubber have been well established especially by the work of Staudinger and his students: *Helv. Chim. Acta*, **5,** 785 (1922); **7,** 23, 842 (1924); **8,** 41, 65, 67 (1925); **9,** 529 (1926); **11,** 1047, 1052 (1928); *Ber.*, **53,** 1073 (1920); **57,** 1203 (1924); **59,** 3019 (1926); **60,** 1782 (1927); **61,** 2427 (1928); **62,** 241, 263 (1929); *Ann.*, **447,** 97, 110 (1926); *Z. physik. Chem.*, **126,** 425 (1927); *Kautschuk*, 237 (1927). For the formulas for cellulose, silk fibroin and rubber see Freudenberg and Braun, *Ann.*, **460,** 288 (1928); Meyer and Mark, *Ber.*, **61,** 593, 1932, 1939 (1928); Meyer, *Naturwissenschaften*, **42,** 790 (1928). The formulas for cellulose and silk fibroin are not, of course, regarded as finally established.

products of these reactions is very meager. That they do not usually proceed intramolecularly follows from the fact that very few large rings are known. It is true that such reactions frequently do not proceed at all under conditions which, in analogous cases, lead to the formation of 5- and 6-rings; but the formation of the latter often proceeds under conditions which do not permit intermolecular reaction even among unifunctional compounds (compare the formation of γ-lactones in the presence of a large excess of water, with the esterification of acetic acid). There are, however, a good many types of reaction which are intermolecular among simple compounds, which are practically free from side reactions, and which by suitable adjustment of experimental conditions may be forced to completion. It should be possible to conduct reactions of these types even when bifunctional, so as to obtain analytically homogeneous products whether they proceed intramolecularly or not. These simple principles have been repeatedly applied to bifunctional reactions in this Laboratory, and they have seldom failed to lead to analytically homogeneous products. Moreover, where the formation of 5- or 6-rings was excluded by the nature of the reacting materials, these reactions have, *without exception,* led to *high polymers.* This fact provides a possible explanation for the meagerness of the information which is available concerning the precise nature of the products of such bifunctional reactions. High polymers frequently have properties which make their investigation very difficult. Moreover, if a chemist is expecting a reaction to lead to materials of simple properties, he is usually inclined to regard the appearance of a resinous or sirupy product which neither can be crystallized nor distilled as signifying only that the experiment has failed. When the products of such reactions have been capable of purification and have shown the expected analytical composition, they have frequently been assumed to be dimeric (and cyclic) for no other reason than that they were obviously not monomeric. In this connection it 'should be emphasized that substances of very high molecular weights may nevertheless be microcrystalline and very soluble (see the following paper).

Some of the points discussed above are illustrated by the following examples.

Anhydrides of the acids of the series $HOOC(CH_2)_xCOOH$ are known in which x has all values from 1 to 8 inclusive. Of these only succinic and glutaric anhydrides are monomeric. These are, respectively, 5- and 6-rings. The other anhydrides which, if monomeric, would be 4-, 7-, 8-, 9-, 10- and 11-rings, are all highly polymeric.[10]

[10] For malonic anhydride see Staudinger and Ott, *Ber.,* 41, 2214 (1908). For the other anhydrides see Voerman, *Rec. trav. chim.,* 23, 265 (1904). The cryoscopic data which Voerman presents on phenol solutions have no bearing on the molecular weights of the anhydrides, since even succinic anhydride reacts rapidly with phenol to form phenyl succinate; Bischoff and von Hedenstrom, *Ber.,* 35, 4076 (1902). Farmer and Kracov-

Hydroxy-acids of the series $HO(CH_2)_xCOOH$ may condense with themselves. Only those in which x is 3 or 4 yield monomeric lactones.[11] These lactones are 5- and Brings, respectively. This series of acids now includes those in which x has all values from 8 to 16 inclusive.[12] The lactones corresponding to the acids in which x has the values 12 to 16 are also known,[12b] as well as the 17-membered lactone of the unsaturated acid, hexadecene-(7)-ol-(16)-acid-(1).[13] All of these lactones are perfectly stable substances and can be distilled without decomposition;[14] and yet none of these lactones has been synthesized by a bifunctional reaction.[15] They were synthesized by the oxidation of the corresponding cyclic ketones with persulfuric acid. By heating the acids, products are indeed obtained which have the same analytical composition as the lactones, but[1]"' they are "polymeric-like." The properties of the known lactones of this series indicate that lactones cannot be intermediates in the formation of these polymers. The formation of these must, therefore, involve C polymerization.

Amino acids of the series $NH_2(CH_2)_xCOOH$ are known in which x has the values 3, 4, 5 and 6. When x is 3 and 4, intramolecular anhydride formation occurs spontaneously at the melting point of the acids, the products being the 5- and 6-membered rings, pyrrolidone and piperidone.[16]

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ski have recently obtained adipic anhydride in a monomeric form, *J. Chem. Soc.*, 680 (1927).

[11] On this point no data are available for those in which x is 5 and 6 [THIS JOURNAL, 46, 2838 (1924); *Ber.*, 60, 605 (1927); *ibid.*, 33, 864 (1900)]. The analogous acids, $CH_3CHOH(CH_2)_2CH(CH_3)CH_2COOH$ [Baeyer and Seuffert, *ibid.*, 32, 3619 (1899)] and $C_2H_5CHOH(CH_2)_4COOH$ [Blaise and Kohler, *Compt. rend.*, 148,1772 (1909)], have been prepared, and by heating are converted at least partially into the 7-membered lactones. The acid $C_2H_5CHOH(CH_2)_5COOH$ has also been prepared. On heating, it also loses water, but the 8-membered lactone is not formed. The product is a lactide-like material which cannot be distilled without decomposition (Blaise and Kohler).

[12] (a) Lycan and Adams, THIS JOURNAL, 51, 625 (1929); (b) Ruzicka and Stoll, *Helv. Chim. Acta.*, 11, 1159 (1928). Since this paper was written a great deal of further information concerning these acids has become available in the paper of Chuit and Hausser, *ibid.*, 12, 463 (1929'1.

[13] Kerschbaum, *Ber.*, 60, 902 (1927).

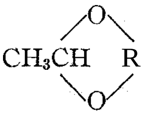
[14] This indicates that large heterocyclic rings are not less stable than their lower homologs. Their physical properties are such as would be expected from the known properties of their lower homologs. The mere presence of a large ring does not result in the development of any of those unusual secondary, residual, or supermolecular forces which are sometimes supposed to confer "polymeric" properties on relatively simple molecules.

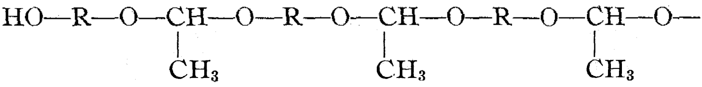
[15] Kerschbaum (ref. 13) records various attempts to prepare ambretollid by the methods commonly used for the preparation of lactones. By heating the acid he obtained traces of an oil which had the odor of the lactone. (It is powerfully odorous.) The product was, however, for the most part, a gelatinous material *soluble* in *alkali*. For the usefulness of the method proposed in German Patent Application 150,677, see Ruzicka and Stoll, ref. 12 b.

[16] Gabriel, *Ber.*, 22,3338 (1889); Schotten, *ibid.*, 21,2240 (1888).

When x is 5 the acid is, on heating, converted to the extent of 20 to 30% of the theoretical into the 7-membered lactam. "The rest of the acid is converted into a viscous gelatinous mass which could be obtained in a state of only approximate purity and which, according to the analysis, is isomeric with the 7-membered lactam; that is, it is a polymeric product."[17] Where x is 6 no trace of the corresponding lactam could be obtained by heating the acid, although this lactam (suberone-isoxime) is a known and stable substance.[18] By heating the acid a product was obtained having the same composition as this lactam, but it was an undistillable solid, insoluble in most solvents.[17]

The compounds $Br(CH_2)_xNH_2$, where x is 4, 5 and 6, react with themselves with the formation of secondary amines containing the structural unit $(—CH_2—)_xNH—$. Where x is 4 and 5 the products are the monomeric 5- and 6-rings, pyrrolidine and piperidine.[19] Where x is 6 the amount of the monomeric base (7-ring) formed was too small to permit purification.[20] The product was for the most part an oil which solidified to a waxy solid. It could not be distilled in vacuum without decomposition, and though no molecular weight determination is recorded, v. Braun seems inclined to regard it as dimeric. Its properties are obviously more consistent with a more highly polymeric structure.

An interesting example of a bi-bifunctional reaction is found in the reaction between glycols and acetaldehyde (or acetylene). This presents the possibility of forming cyclic acetals, , or polyacetals,



$$HO—R—O—\underset{\displaystyle CH_3}{\underset{|}{CH}}—O—R—O—\underset{\displaystyle CH_3}{\underset{|}{CH}}—O—R—O—\underset{\displaystyle CH_3}{\underset{|}{CH}}—O—$$

, etc. This reaction has been studied by Hill and Hibbert.[21] Ethylene and trimethylene glycols gave in excellent yields the cyclic acetals which are 5- and Brings. Tetramethylene glycol gave in poor yield a volatile compound which was apparently the monomeric cyclic acetal containing a 7-ring. A considerable part of the product was an undistillable sirup. The products from octamethylene and decamethylene glycols were also undistillable sirups. No molecular weight determinations are recorded. Hill and Hibbert

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[17] V. Braun, *Ber.*, 40, 1840 (1907).

[18] B. p. 156° at 8 mm. It is, however, not prepared by a bifunctional reaction, but from cycloheptanone oxime by the Beckmann rearrangement. Wallach, *Ann.*, 312, 305; 309, 18 (1899).

[19] V. Braun and Beschke, Ber., 39, 4121 (1906); Blank, ibid., 25, 3044 (1892); V. Braun and Steindorf, *ibid.*, 38, 172 (1905).

[20] V. Braun and Steindorf, *ibid.*, 38, 1083 (1905); v. Braun, *ibid.*, 43,2853 (1910).

[21] Hill and Hibbert, THIS JOURNAL, 45, 3108, 3124 (1923). See also Franke and Gigerl, *Monatsh.*, 49, 8 (1928).

recognized of course that these sirups might have the polymeric linear structure indicated above, but seemed inclined to regard them as simple rings of a peculiar kind.

The only reaction which has led to the formation of large carbon rings from open-chain compounds is the action of heat on certain salts of dibasic acids.[22] In no case are these large rings the chief products of this reaction, nor can it be established that they are primary products, since the reaction takes place at high temperature. If polymeric products were formed they would be decomposed thermally. High polymers could not appear in the distillate from which the products are isolated, because high polymers cannot be distilled. These features sharply distinguish this reaction from other truly bifunctional reactions which might, but which do not, so far as our information goes, lead to rings of the same type.[23]

Any theory which attempts to explain why 5- and 6-rings are formed very readily and larger rings with very great difficulty must take into account the fact that these larger rings are not less stable than the smaller. A satisfactory theory is already available. The Baeyer strain theory in its original form is made untenable by the existence of the higher cyclopar-affins, and has been replaced by the Sachse–Mohr theory which permits the existence of non-planar and strainless rings and which has besides a great deal of other evidence in its support.[24] The features of this theory essential to the present argument are exceedingly simple. They involve the assumption of the tetrahedral angle in the carbon valences and of free rotation about each carbon–carbon single bond in a chain. No description of stereochemical relations can be as convincing as a demonstration with suitable models.[25] Such models show that there is a certain inevitability in the formation of 5- and 6-rings and a large degree of fortuity in the formation of larger rings. This question has been considered in some detail by Mohr.[26] Regarding the possibility of the forma-

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[22] Ruzicka and co-workers, *Helv. Chim. Acta*, 9, 230, 249, 339, 389, 399, 499, 715, 1008 (1926); 10,695 (1927); 11,496,670,686, 1174, 1159 (1928).

[23] For example, the action of metals on a dihalide, $Br(CH_2)_xBr$. Thus decamethylene bromide reacts rapidly and very smoothly with metallic sodium, but no cyclodecane is formed. See Franke and Kienberger, *Monatsh.*, **33**, 1189 (1912). This reaction will be discussed in a later paper.

[24] See Huckel, "Der gegenwärtige Stand der Spannungstheorie," *Fortschritte Chem. Physik und physik. Chem.*, Band 19, Heft 4, 1927.

[25] Ordinary (preferably quite small) wire tetrahedra may be joined by short pieces of rubber tubing in such a way that the arms which are being connected over-lap. This provides free rotation about the union, but prevents bending. This method of union insures that any model which is built up is practically strainless (*i. e.*, the tetrahedral angle is always retained) and at the same time is sufficiently mobile to illustrate the multiplicity of forms which long chains and large rings can assume.

[26] Mohr, *J. prakt. Chem.*, 98,348 (1918).

tion of a cyclic ketonic ester by the internal condensation of sebacic ester he says:

> The molecule of sebacic ester is a very long chain. The multiplicity of forms which this molecule can assume is extraordinarily great. It is clear that by the random collisions of the molecuies, fewer molecules of sebacic ester will in unit time assume the form necessary for ring closure than is the case with adipic ester under the same conditions, since this contains in its molecule only four methylene groups, and four less points of rotation than does sebacic ester. To bring the two ends of the sebacic ester molecule together in the least forced fashion apparently requires a very small amount of energy or none at all. Unfortunately, however, we have not the means arbitrarily and with the least possible expenditure of energy to bring about the desired change in form of the molecules and to hinder the undesired. In this connection we are left entirely to chance, that is, to random collision, which will bring about a given form the more rarely the more forms are possible, *i. e.*, the longer the chain between the two carboxyl groups.

In perhaps two dozen cases it is well established that a bifunctional reaction proceeds fairly smoothly with the formation of a larger-than-6-ring. These cases include more 7-membered than larger rings, and more aromatic than aliphatic compounds. The Sachse–Mohr theory would lead one to expect that the formation of 7-rings would not be very much more difficult than the formation of 6-rings. The bifunctional reactions discussed in the examples offered above all involve purely aliphatic compounds, and for the most part the chains are unsubstituted. In most of these examples the formation of a 7-ring occurs to a certain extent, and the formation of the corresponding 8-ring not at all. It appears that in such 7-atom chains the probabilities of intra- and intermolecular reaction are about equal. The addition of one more atom to the chain diminishes the probability of intra- with respect to intermolecular reaction to such an extent that only the latter appears. These relations may be somewhat modified by the presence of substituents on the chains and even by the nature of the reacting groups in ways which it is, at present, impossible to predict. It is evident, however, that if two atoms of such a chain are adjacent atoms of a benzene ring their position with respect to each other is fixed, and the chances of intramolecular reaction are greater than in an analogous simple chain of the same length. (The latter will have one more axis of rotation than the former.) It is therefore not surprising that in $NH_2(CH_2)_6Cl$ intramolecular reaction occurs only to a slight extent, and in *o*-$NH_2C_6H_4(CH_2)_4Cl$ almost quantitatively.[27] Other similar examples might be cited.

There is also some evidence to indicate that even simple substituents such as methyl groups on a chain may increase the tendency toward the formation of larger rings.[28] Researches in the diphenyl series have established that substituent groups suitably placed may completely inhibit

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[27] v. Braun and Bartsch, *Ber.*, **32**, 1270 (1899).

[28] See "Annual Reports of the Progress of Chemistry," **1927**, p. 100; Moyer and Adams, THIS JOURNAL, **51**, **630** (1929).

rotation about a nearby single bond, and a similar effect in aliphatic chains is at least conceivable. Any restriction of the freedom of rotation of the atoms of a chain would, on the basis of the Sachse–Mohr theory, increase the chances of ring formation.

The process of polyintermolecular condensation finds no mention in treatises on polymerization. This may be due to the fact that such a process is not admitted to exist, or that it is not admitted to be polymerization. The examples cited above, and others to be described later, prove that such a process does exist, and that it may result in the formation of very large molecules. Whether it is to be regarded as polymerization or not will depend upon the definition which is adopted for that term. The definitions offered above include it as a special type of polymerization. This classification'finds more to justify it than the analogies which are recognized in these definitions.

The process of A polymerization (the only type which appears to have been generally recognized) results in the formation of large molecules from small; and it has come about that any process which has this result is called polymerization. Since, however, A polymerization is by definition a process of self-addition, chemists have often been misled to the assumption that condensation leads directly only to small molecules, and that if large molecules are formed from small as the apparent result of condensation, this is due to the intervention of some unsaturated molecules capable of undergoing A polymerization.[29] It is quite certain, however, that in many such cases (*i. e.*, in all cases of true C polymerization) no such intermediate products occur. This is a matter of important practical implications. The reactions involved in the formation of A polymers must, in the nature of the case, be for the most part reactions which are peculiar to the process of polymerization. For this reason the mechanism of A polymerization still remains somewhat obscure. Hence, the mere assumption that unsaturated intermediates intervene in a reaction which leads to high polymers contributes little to one's understanding of the mechanism of the process, or the structure of the product. In those cases in which this assumption is wrong its use leads one to regard as complicated and

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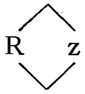
[29] Thus, Drummond, *Inst. Rubber Ind.*, 4, **43** (1928), states, "Where resins are formed by a preliminary condensation as are the phenol-formaldehyde products, it is logical to assume that in the preliminary reaction, unsaturated atomic linkings are introduced which provide the necessary arrangement for polymerization subsequently to occur." Scheiber, *Chem. Umschau, Fette, Oele, Wackse Harze,* 15,181 (1928), is even more explicit: "Für den Aufbau organischer Stoffe kommen bekanntlich nur zwei Prozesse in Betracht, und zwar Kondensationen und Polymerisationen. Vorgange der ersterep Art fuhren im allgemeinen zu Molekulverbänden beschränkter Grösse—. . Bei Polymerisationen hingegen kommt es in manchen Fallen zur Ausbildung extrem grosser Moleküle. . ."

mysterious a process which may be simple and obvious. C polymerization merely involves the use in a multiple fashion of the typical reactions of common functional groups. Among bifunctional compounds these reactions may proceed in such a way as to guarantee the structure of the structural unit, —R—, in the polymer, $(\text{—R—})_n$, formed. It is one of the immediate objects of the researches to be described in subsequent papers to discover how the physical and chemical properties of high polymers of this type are related to the nature of the structural unit.

Summary

Linear polymers conform to the type —R—R—R—R—R—, etc., which is characterized by a recurring structural unit. The structural unit —R— is a bivalent radical. Two types of polymers are recognized. (1) Addition or A polymers: the polymeric molecule is converted by heat into a monomer having the same composition as the structural unit, or the polymer is formed by the mutual addition of a number of such monomers. (2) Condensation or C polymers: the polymeric molecule is converted by hydrolysis or its equivalent to a monomer which differs in composition from the structural unit by one H_2O (or HCl, NH_3, etc.), or the polymeric molecule is formed from numbers of the monomers by a process of polyintermolecular condensation. Rubber, polystyrene, polyoxymethylene and paracetaldehyde are A polymers. Cellulose, silk fibroin and hexa-ethylene glycol are probably C polymers.

Substances of the type x—R—x and x—R—y are called bifunctional. In these formulas —R— represents a bivalent radical and x and y functional groups capable of reacting with each other in a known fashion to form the new functional group, z. Reactions of the type x—R—y ⟶ *product* are called bifunctional and those of the type x—R—x + y—R—y ⟶ *product* are called bi-bifunctional. Such reactions will lead to compounds containing the structural units —R—z— and —R—z—R—z—. Bifunctional reactions will be intramolecular and will lead to the monomeric product,  when this can be a 5- or 6-ring. If the monomeric product can only be a larger-than-6-ring, reaction will usually be intermolecular and the product a polymer of the type —R—z—R—z—R—z—R—z—R—z—, etc.

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STUDIES ON POLYMERIZATION AND RING FORMATION. II. POLY-ESTERS

BY WALLACE H. CAROTHERS AND J. A. ARVIN

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An example of a bi-bifunctional reaction is found in the reaction between a dibasic acid and a dihydric alcohol, $HOOC—R'—COOH + HO—R''—OH$, which, if it is conducted so as to involve both functional groups of each reactant, must lead to an ester having the structural unit, $—OC—R'—CO—O—R''—O— = —R—$. In accordance with the thesis developed in the previous paper, esters formed in this way will be polymeric unless the number of atoms in the chain of the structural unit is less than seven. In this paper esters are described in which the number of atoms in the chain of the structural unit is 7, 8, 9, 10, 11, 12, 14, 15, 16, 18. and 22 atoms. All these esters are highly polymeric, and, although some of them have been prepared by various methods, no monomeric form of any of them has as yet been isolated.

Preparation of the Esters

The following method was used for the preparation of the solid esters whose properties are listed in the table. The acid together with a 5% excess of the glycol was placed in a Claisen flask provided with a receiver and condenser, and the flask was heated in a metal-bath. At about 160° (bath temperature) reaction set in. Water distilled off freely during the first hour (temp., 175-185°) and very slowly if at all during the succeeding two hours at the same temperature. The receiver was now changed, the flask provided with a very fine capillary and heating continued under a good vacuum (usually less than 0.2 mm.) for about three hours, the temperature of the bath being raised to 200–250°. During this period little or no distillate collected (provided only a 5% excess of glycol was used). The residue, which was a slightly dark and, at 150°, more or less viscous liquid, was poured from the flask. The amount of this residue corresponded with the theoretical (based on the acid used), and the amount of water actually collected approached the calculated more closely the larger the sample used (60–90%). The esters were purified by crystallization.

Ethylene malonate was prepared by heating ethyl malonate and glycol in the same fashion. There was some decomposition (evolution of gas) when the residue was heated to 240° in *vacuo.* This residue was a thick sirup which could not be induced to crystallize. It was dissolved in acetone, filtered and heated for several hours at 175–190° in high vacuum. Nothing corresponding to a monomeric ethylene malonate was found on redistilling the distillates from this preparation.

The preparation and properties of some esters not included in the table are described in the Experimental Part of this paper.

Structure of the Esters

The conclusion that these compounds are esters and that they contain the structural unit —R— indicated above follows directly from the method of preparation and is supported by the analytical data and chemical behavior. Comparison of Cols. 4 and 5 in Table I shows that the carbon and hydrogen percentages in general agree with those calculated for —R—. So also did saponification numbers where these were determined. The products of saponification of the esters are the acids and glycols from which they were prepared.

That the esters are not monomeric 7-, 8-, 9-, . . ., 22-membered rings is indicated by their physical properties and by their molecular weights. In Col. 7 are given the molecular weights calculated from the observed boiling point elevations or freezing point lowerings, and in Col. 8 the solvents and methods used. The solvents used in the ebullioscopic determinations include chloroform, ethylene chloride, benzene and acetone. Those used in the cryoscopic determinations include benzene, glacial acetic acid and diphenyl ether.

In these determinations it was necessary to use rather large samples to obtain boiling point or freezing point changes of 0.02 to 0.05°. Judged by their self-consistency, the values obtained with the use of freezing benzene have about the same relative accuracy as is ordinarily attained with simple compounds. With other solvents, and especially in the boiling point determinations, observations were much less consistent. This was due in part at least to changes of surface tension, associated no doubt with molecular size, since there was much foaming. The values obtained by this method are recorded, since for some of the esters they are the only ones available, and for others they clearly indicate that the order of magnitude of the apparent molecular weights is quite independent of the character of the solvent used.

The lowest molecular weight observed for any of the solid esters was 2300 and the highest 5000. The mean of all the determinations is 3200, and for purposes of calculation the molecular weight of each ester has been assumed to be approximately 3000. Such a molecular weight corresponds with a value of 8 to 20 (depending on the length of the chain of the structural unit) for n in the general formula $\text{—(—CO—R}'\text{—CO—O—R}''\text{—O—)—}_n$. It can scarcely be supposed that the molecules present in a given sample are all identical so far as the values of n are concerned, but their crystallinity and a certain homogeneity in such physical behavior as solubility indicate that the varieties of molecular species present in a given sample probably do not include a very wide range.

The disposition of the valences at the ends of the chains in the above formula cannot as yet be definitely decided. A cyclic structure is rendered improbable by the same considerations which led us to expect that these esters would be polymeric and which have been discussed in the previous paper. Esters prepared by the method indicated above are definitely not acidic, and since the detection of a carboxyl group in a molecule having a weight of 3000 to 5000 should present no difficulties, no carboxyl groups can be present at the ends of the chains. Attempts to detect the presence of hydroxyl groups have not as yet succeeded. Ethylene succinate crystallizes unchanged from acetic anhydride, and is not affected by phenyl or naphthyl isocyanate. Nevertheless we are inclined to assume that hydroxyl groups are present at each end of the chain due to the presence of one more molecule of glycol than acid: $HO—R''—O—(—CO—R'—CO—O—R''—O—)_n—H$. The failure of these groups to react with reagents may be ascribed to the operation of the same factors which set a limit to the size of the molecules formed.

In general the analytical values agree more closely for such a formula than for a cyclic formula. In Col. 6 of Table I are given the carbon and hydrogen percentages calculated for this formula assuming a molecular weight as close as possible to 3000. The means of the deviations between the carbon and hydrogen percentages found and those calculated for the —(—R—)—, formula are –0.48 and –0.01%; while the deviations calculated for the $HO—(—R—)_n—R'—OH$ formula are –0.31 and –0.11%.

Assuming a molecular weight of 3000 the chains, $H—[—O—(CH_2)_y—O—CO—(CH_2)_x—CO—]_n—O—(CH_2)_y—OH$, would contain 170–200 atoms and their lengths would lie between 249 and 280 Å.[1] Their lengths are therefore of the same order of magnitude as that assumed by Meyer[1] for the cellulose chains (100 glucose units per chain = 510 Å.). The molecular cohesions calculated from the data presented by Meyer[2] lie between 250,000 and 300,000 cal. or 3.3 to 4 times the heat of separation of a carbon-carbon bond (75,000 cal.). These molecular cohesions are, however, only about 10% of those calculated for a cellulose chain of 500 Å.

The structure of these esters will be discussed in more detail later in the light of experimental work which is not yet completed.

Properties of the Esters

All the esters of the type $—(—CO—(CH_2)_x—CO—O—(CH_2)_y—O—)—$ with the exception of ethylene malonate are crystalline solids. The property of crystallinity is not very highly developed, but it is quite definitely present.[3] This fact is of interest because examples of crystalline highly polymeric substances are not very numerous. As with all crystalline substances of this class, it is not possible to develop large crystals. Ethylene succinate when it separates from a melt or from concentrated solutions (in chloroform) crystallizes in doubly refracting spherolites (microscopic) which grow to what appear to be star-like groups of needles.

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[1] The values C = 1.5 Å. and O = 1.1 Å. are taken from Meyer, *Naturwissenschaften,* 42, **782** (1928).

[2] Ref. 1, p. 790.

[3] So far as they have been examined in this respect, all these esters give sharp x-ray diffraction patterns.

Table I

Poly-esters

Compound	Formula of structural unit —R—	Atoms in chain of str. unit	Analyses				Anal. calcd. for HO—(R)$_n$—R″—OH assuming for M. w. the nearest value to 3000				App. mean M. w. obs.	Solvent and method	M. p., °C.
			Found, % C	Found, % H	Calcd. for —R—, % C	Calcd. for —R—, % H	C, %	H, %	n	M. w.			
Ethylene malonate	$-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O-(CH_2)_2-O-$	7	46.42 46.46	4.85 4.84	46.15	4.65					2700, 2500 3500, 2700, 2300	B. p., AcMe, B. p., CHCl$_3$	Liquid
Ethylene succinate	$-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O-(CH_2)_2-O-$	8	49.75 49.82	5.71 5.61	49.97	5.58	49.75	5.69	20	2943	3400, 3500, 2500 2900, 2500, 2300	B. p., CHCl$_3$ B. p. (ClCH$_2$)$_2$	108
Trimethylene succinate	$-\overset{\overset{O}{\|}}{C}-(CH_2)_2-\overset{\overset{O}{\|}}{C}-O-(CH_2)_3-O-$	9	52.95 52.72	6.45 6.32	53.13	6.38	52.99	6.48	19	3080	4300, 3500 3600, 3900	F. p., AcOH B. p ., C$_6$H$_6$	52
Ethylene adipate	$-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-O-(CH_2)_2-O-$	10	55.23 55.28	7.08 7.06	55.78	7.03	55.42	7.08	17	2988	3400	F. p., AcOH	50
Trimethylene adipate	$-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-O-(CH_2)_3-O-$	11	57.42 57.21	7.62 7.50	58.03	7.58	57.76	7.66	16	3054	2700, 2900 2700 3600, 3300, 3200 4300, 2400	F. p., C$_6$H$_6$ B. p., C$_6$H$_6$ F. p., AcOH	45
Hexamethylene succinate	$-\overset{\overset{O}{\|}}{C}-(CH_2)_2-\overset{\overset{O}{\|}}{C}-O-(CH_2)_6-O-$	12	59.41 59.32	7.95 7.92	59.97	8.05	60.00	8.22	14	2920	3200, 3500	B. p., C$_6$H$_6$	57
Hexamethylene adipate	$-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-O-(CH_2)_6-O-$	14	62.67 62.57	8.82 8.86	63.10	8.85	63.09	8.96	13	3084	3300	F. p., AcOH	56
Ethylene sebacate	$-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-O-(CH_2)_2-O-$	14	62.37 62.38	8.96 8.81	63.10	8.85	62.62	8.86	13	3028	3100, 3100	F. p., C$_6$H$_6$	79
Trimethylene sebacate	$-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-O-(CH_2)_3-O-$	15	64.20	9.09	64.41	9.17	63.98	9.20	12	2982	4600, 5000 3100, 3100	B. p. (ClCH$_2$)$_2$ F. p., C$_6$H$_6$	56
Decamethylene succinate	$-\overset{\overset{O}{\|}}{C}-(CH_2)_2-\overset{\overset{O}{\|}}{C}-O-(CH_2)_{10}-O-$	16	64.62 64.67	9.53 9.28	65.57	9.45	65.78	9.63	11	2992	3500, 3400, 3200	B. p., C$_6$H$_6$	68
Hexamethylene sebacate	$-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-O-(CH_2)_9-O-$	18	66.72 66.97	9.81 9.94	67.56	9.92	67.30	10.01	10	2960	2700, 2600	F. p., C$_6$H$_6$	67
Decamethylene adipate	$-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-O-(CH_2)_{10}-O-$	18	67.23 67.01 67.27	9.82 9.93 9.94	67.56	9.92	67.64	10.09	10	3016	3300, 3200	F. p., C$_6$H$_6$	77
Decamethylene sebacate	$-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-O-(CH_2)_{10}-O-$	22	70.32 70.76	10.70 10.73	70.53	10.67	70.44	10.79	8	2896	3000, 3000	F. p., C$_6$H$_6$	74

From dilute alcohol solutions it separates in discrete microscopic needles.[4]

Crystallized ethylene succinate and decamethylene sebacate are dusty powders which have a great tendency to become electrified. Some of the intervening members are quite soft and even somewhat sticky. Ethylene succinate solidifies from a melt as a hard, brittle, opaque, white mass. Decamethylene sebacate solidifies to a white, brittle, waxy solid.

The non-crystalline members include ethylene malonate, ethylene fumarate and ethylene, trimethylene, hexamethylene and decamethylene phthalates. The phthalates and the fumarate evidently have less symmetry than the saturated straight-chain purely aliphatic type. The lack of crystallinity of the malonate may be associated with the low melting point of the malonic acid; or it may be due to the fact that considerable decomposition occurred during the process of esterification.

The melting points of the solid esters are not very sharp and they depend somewhat upon the rate of heating. This latter effect is noticed especially with ethylene succinate.

When the crude reaction mixture is dissolved in chloroform and precipitated with benzene, the resulting dusty white powder melts in a capillary tube at about 102". If, however, the tube is placed in a bath which has already been heated to 96° the sample melts at once. The two melting points are called the slow and instantaneous melting points, respectively, and they are best observed on a bloc Maquenne. Samples which are dusted on the bloc when it is below 96° do not melt until it reaches 102°, but as soon as the bloc reaches 96" samples melt the instant they touch it. Both these temperatures may be changed somewhat by repeated crystallization, but a sample whose melting point has been raised by repeated crystallization may suddenly show the original melting point on further crystallization. By long extraction with boiling absolute alcohol in which it is practically insoluble, ethylene succinate is modified so that the instantaneous and slow melting points coincide at about 107–108°, and from the extracts may be isolated a very small amount of lower-melting material. When such a high-melting sample is again crystallized from a mixture of chloroform and benzene or ether, the melting point usually drops, and one observes again the instantaneous melting point of 96" and the slow melting point 102°. The melting point of such samples may also be raised by long heating just below 100°, and both melting points then gradually approach 107°. When a 96, 102° sample is quickly melted, then allowed to solidify in an agate mortar and powdered, the instantaneous melting point is lowered somewhat, and the slow melting point may be either raised or lowered, depending upon the time during which the molten material is heated.

Attempts to define the melting point more clearly by heating or cooling curves on fairly large samples were unsuccessful.[5] Apparently the viscosity of the melt is so great

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[4] Incidentally these are the forms in which Hess' trimethylcellulose crystallizes, and the photomicrographs (Figs. 78, 80 and 81) which he presents ("Die Chemie der Zellulose," Leipzig, 1928, p. 432) for this substance would serve almost perfectly as pictures of ethylene succinate. The crystallinity of this trimethylcellulose therefore provides no guarantee either than it contains only a single molecular species, or that the molecules present are not very large.

[5] Some experiments were kindly made for us by Dr. E. L. Skau with the special apparatus which he has devised for the precise determination of the melting points of pure organic compounds.

as to make the process of crystallization slow even in the presence of previously formed crystals and under a considerable temperature gradient.

The erratic behavior of the melting points may be associated with the fact that all these esters are hygroscopic, but the absorption of water cannot be the sole cause for this behavior, for samples of ethylene succinate having various melting points were stored over 20% sulfuric acid for ten days and all of them gained considerably in weight without changing in physical appearance or melting point.

Anomalies in melting points are not unknown among compounds of definite constitutions and relatively low molecular weights. One may cite, for example, the fact that sucrose separates from methyl alcohol in crystals melting at 169–170° and from other solvents in crystals melting at 179–180°, and these two forms do not show any detectable chemical differences.[6] But the case of ethylene succinate appears to be more complicated and confused than this. Its melting point depends upon its history in a fashion which can as yet be defined only to the following extent—it always rises and approaches 107° as it is, while still in the solid state, heated or extracted with boiling absolute alcohol.

Among the other esters these irregularities were less pronounced. Nevertheless, the melting points are not very characteristic and no attempt was made to crystallize them to constant melting points. Instead they were crystallized two to six times depending upon the color and softness of the sample. The melting points recorded are the highest observed for complete melting and are usually within 5° of the lowest observed for any sample of the same material. The melting range was usually less than 2°. The melting point of the decamethylene ester of a given acid was higher than that of the hexamethylene ester. The melting point of the hexamethylene ester was higher than that of the trimethylene ester, which was in turn lower than that of the ethylene ester. With one exception, the adipic ester of each glycol melted lower than either its succinic or sebacic ester.

All of these esters are, when molten, quite viscous. Those which do not crystallize on cooling become more or less hard, tough and glassy. The use as resins of esters formed by the action of polybasic acids on polyhydric alcohols has been covered by numerous patents.[7] The impression seems to prevail that all such esters are resins. Of the esters described in this paper the majority are crystalline. The phth: lates which we have prepared are, however, all resinous. Ethylene phthalate is quite tough and moderately hard. Neither this ester nor the trimethylene, hexamethylene nor decamethylene esters of the same acid have been described in the scientific literature. As the length of the alcohol chain increases, these phthalates become progressively softer. Decamethylene phthalate has the cousistency of a moderately thick sirup.

None of these esters is volatile. Each of them has been heated to

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[6] Pictet and Vogel, *Helv. Chim. Acta,* 11, 901 (1928).

[7] See for example U. S. Patents Nos. 1,108,332; 1,091,627; 1,091,628; 1,091,732 1,108,329; 1,108,330; 1,108,331; 1,642,079; 1,678,105; 1,098,776; 1,098,777; 1,424,137; 1,413,144; 1,413,145; 1,667,199; 1,667,200; 1,119,592; 1,141,944; 1,663,183.

200° in *vacuo* without showing any tendency to distil. Ethylene succinate heated for three hours at 250° under a pressure of 2 mm. is not changed in properties, and its analytical composition (carbon, hydrogen and saponification number) is not changed. It shows no tendency to distil or to evolve any volatile products when heated to 280° at a pressure of 1 micron. At 350° ethylene succinate undergoes complete thermal decomposition, the products being ethylene, acetaldehyde, succinic anhydride, carbon, etc.[8]

All of these esters are insoluble, or nearly so in water, alcohol, petroleum ether and ether.[9] The least soluble of the saturated aliphatic esters is ethylene succinate. It is more or less soluble in hot ethyl acetate, acetic acid, acetic anhydride, ethyl succinate and acetone, and it crystallizes from these solvents on cooling. It is insoluble in benzene. The other saturated aliphatic esters with the exception of ethylene malonate are readily soluble in cold benzene and at least moderately soluble in acetone, ethyl acetate and glacial acetic acid. The solutions are noticeably viscous only when fairly concentrated (e. g., 10% or stronger). This fact and the rapidity with which solution occurs lead us to believe that the solutions are true molecular dispersions.

Although none of these esters is soluble in water they are all somewhat hygroscopic. This property is especially pronounced in those poly-esters which are not crystalline. The drying of these resins was very difficult and, as the analytical results indicate, was not always successful. Drying to constant weight was complicated by the tendency to foam when heated in *vacuo*.[10]

Other Methods of Preparation

The only detailed study of poly-esters of the type here described which we have found is reported in a paper by Vorländer.[11]

Ethylene succinate was first prepared by Lourenço[12] by heating succinic acid and ethylene glycol to 300° (m. p. about 90"). Subsequently Davidoff[13] prepared Lourenço's ester and identified it with one which he obtained by heating silver succinate with ethylene bromide. Vorländer

[8] Tilitschejew, *J. Russ. Phys.-Chem. Soc.*, *57*, 143 (1925).

[9] It is interesting to note that Freudenberg and Braun's trimethylcellulose, like ethylene succinate, is insoluble in ether and carbon tetrachloride, but quite soluble in chloroform [*Ann.*,460,288 (1928)].

[10] It is interesting to observe that inulin, a polymeric substance of a different type, but probably of the same degree of molecular complexity as the esters here described is also quite hygroscopic. *Cf.* Drew and Haworth, J. *Chem. Soc.*, 2690 (1928).

[11] Vorländer, *Ann.*, 280, 167 (1894). See also Bischoff, *Ber.*, 27, 2940 (1894); 40, 2779, 2803 (1907). Glycol esters of adipic acid are referred to in German patent 318,222, *Chem. Zentr.*, II, 536 (1920).

[12] Lourenço, *Ann. chim. phys.*, 293 (1863).

[13] Davidoff, *Ber.*, 19,406 (1886).

studied this latter compound in detail and showed that its chemical behavior was in all respects what would be expected of an ethylene ester of succinic acid. He also identified it with Lourenço's ester and with one obtained by the action of succinyl chloride on the disodium derivative of ethylene glycol.

Vorlander found that his ethylene succinates prepared from silver succinate and from succinyl chloride had apparent molecular weights ranging from 265 to 321 in freezing phenol and in freezing acetic acid. He supposed them to be dimeric, and in accordance with this view was able to prepare the same compound from silver succinate and di-(β-chloro-ethyl)-succinate. This method of synthesis evidently merely establishes that the compound was probably not monomeric.

The properties which Vorlander records for ethylene succinate agree in general with those which we have observed. We have found that it is possible to prepare ethylene succinates having, within certain limits, various melting points (and molecular weights) by heating succinic acid and glycol in various proportions. The highest melting (102") is that described above. It was prepared from acid and excess glycol. Vorlander and other writers on this subject ascribe to ethylene succinate a melting point of 88–90". We have obtained samples showing this melting point by using the acid and glycol in equivalent amounts; and, by using excess acid, have obtained lower-melting samples. These ethylene succinates differ somewhat in solubility, but they are alike in physical appearance, in their lack of volatility and in their viscpus character when molten. All of these materials are highly polymeric. We have also prepared ethylene succinate from silver succinate and ethylene bromide according to Vorlander's directions. This reaction does not proceed smoothly, and our product was slightly colored and melted at 75° instead of at 90°. Nevertheless, molecular weight determinations in boiling ethylene chloride gave values ranging from 1400 to 2000. We think, therefore, that Vorlander's molecular weight determinations must be in error; and this conclusion is supported by the fact that the properties which he records and which we have observed are not consistent with so low a molecular weight as 288.

We have also prepared ethylene succinate from ethyl succinate and glycol. It is also highly polymeric. Thus the methods which have been used for the preparation of this compound include four separate and distinct methods commonly used in the preparation of esters. They all lead to products of the expected composition but of high molecular weights. There is not the slightest reason for supposing that the monomeric ethylene succinate should be incapable of existence, or even that it should be unstable, but it still remains unknown. These facts find their explanation in the thesis developed in the previous paper.

Vorlander also prepared ethylene maleate and ethylene fumarate by the silver salt method. He could not obtain any consistent values for the molecular weights of these materials. We have prepared the fumarate from ethyl fumarate and the maleate from maleic anhydride. Our preparations differ from those of Vorlander in several respects. Thus, our maleate was crystalline and our fumarate resinous. The reverse was true for Vorlander's compounds. Neither our analytical values nor his agree well with the calculated. These esters appear to be much more complicated in their behavior than ethylene succinate. They both become completely insoluble on heating.

Experimental Part

Ethylene Phthalate **No.** 1.—Ethylene glycol 62 g. (1 mole) and phthalic anhydride 74 g. (0.5 mole) were heated together for eight hours at 190° under ordinary pressure and for three hours at 300° under 3 mm. The viscous residue was heated with boiling water for twenty minutes, dissolved in chloroform, filtered and precipitated with ether, and then dissolved in acetone, filtered and precipitated with water. It was then dried by heating to 160–170°. The resulting glassy resin was fairly hard when cold, and became softer on heating. All attempts to induce it to crystallize failed. It was neutral: 2 g. required 0.03 cc. of 0.23 N NaOH for alkalinity toward phenolphthalein. It was soluble in chloroform, acetone, ethyl acetate and acetic acid; insoluble in petroleum ether, ether, benzene, alcohol and water.

Anal. Substance dried to constant weight in high vacuum at 70°. Calcd. for $C_{10}H_8O_4$: C, 62.48; H, 4.19; molecular weight, 192; saponification number, 96. Calcd. for $H[O(CH_2)_2OOCC_6H_4CO]_{25}O(CH_2)_2OH = C_{252}H_{206}O_{102}$: C, 62.15; H, 4.28; molecular weight, 4864; saponification number, 97.3. Found: C, 61.86, 61.95; H, 4.29, 4.30; molecular weight by micro boiling point method in ethylene chloride, 4830, 5070, 4680, 4690; saponification number, 95.7.

Ethylene Phthalate **No.** 2.—This was prepared in the same way as No. 1, but with a 20% excess of phthalic anhydride and was purified in a similar fashion. Appearance and solubility were the same as for No. 1.

Anal. After drying to constant weight in high vacuum at 70°. Found: C, 62 11, 62.07; H, 4.29, 4.33; molecular weight, by method of Menzies and Wright in ethylene chloride, 2940, 2700, 3020; by micro boiling point method in ethylene chloride, 3030, 2930; saponification number, 96.2.

Ethylene Phthalate **No.** 3.—Prepared by heating diethyl phthalate (0.5 mole) with ethylene glycol (1 mole) in the same fashion and purified as before. Appearance and solubility were the same as for No. 1.

Anal. after drying to constant weight in high vacuum at 70°. Found: C, 62.35, 62.14; H, 4.40, 4.37; molecular weight, by freezing point lowering in diphenyl ether, 2070, 2030; by method of Menzies and Wright in ethylene chloride, 1990, 2100, 2050, 1770; by micro boiling point method in ethylene chloride, 2100, 1870.

Ethylene Phthalate **No.** 4.—This was prepared by stirring vigorously 19 g. of glycol (added slowly) with 60 g. of phthalyl chloride and 51 g. of dry pyridine in 125 cc. of chloroform at 0–5°. The reaction mixture was washed thoroughly with dilute acid and dilute sodium carbonate and water, and decolorized with Darco. After drying the chloroform solution the ester was precipitated with ether. The yield was 53 g. It resembled the other ethylene phthalates, but its solutions in chloroform were less viscous —0.016 poise for a 20% solution at 27° as compared with 0.027–0.031 poise for the other ethylene phthalates. Its apparent molecular weight was also lower.

Anal. after drying to constant weight in high vacuum at 70°. Found: C, 61.64, 61.64; H, 4.28, 4.30; molecular weight, by method of Menzies and Wright in ethylene chloride, 1550, 1610; saponification number, 99.5, 99.6.

Hydrolysis of Ethylene **Phthalate.**—Twenty grams of ethylene phthalate was refluxed for sixty-four hours with 60 g. of 48% hydrobromic acid. After neutralization with sodium carbonate, the reaction mixture was steam distilled, From the distillate was isolated 16.7 g. or 86.6% of the calculated amount of ethylene bromide, b. p. 131–134'. The residue on acidification gave 16.3 g. or 93.6% of the calculated amount of phthalic acid. This on conversion to the anhydride melted at 130–131°.

Trimethylene **Phthalate.**—Seventy-four grams (0.5 mole) of phthalic anhydride and 38 g. (0.5 mole) of trimethylene glycol were heated at 250° for two hours under ordinary pressure and under diminished pressure for two hours. The residue was dissolved in benzene, treated with Darco, filtered and precipitated with ether. When cold it was a clear, glassy solid, somewhat softer than ethylene phthalate. It was soluble in chloroform, benzene, acetone, ethyl acetate and acetic acid; slightly soluble in alcohol; insoluble in ether, petroleum ether and water.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.08; H, 4.89; molecular weight, 206. Calcd. for $H[OOCC_6H_4COO(CH_2)_3]_{15}O(CH_2)_3OH = C_{168}H_{158}O_{62}$: C, 63.63; H, 5.05; molecular weight, 3168. Found: C, 63.68, 63.51; H, 5.17, 5.12; molecular weight by micro boiling point method in ethylene chloride, 3180, 3030.

Hexamethylene **Phthalate.**—Twenty-nine and six-tenths g. of phthalic anhydride and 23.6 g. of hexamethylene glycol were heated to 180–190° under atmospheric pressure for two and one-half hours and then for one and one-half hours at 250° under 5 mm. In addition to the water, some phthalic anhydride collected in the receiver. The residual dark gum was purified by dissolving in benzene, decolorizing with Darco, and precipitating with ether. It formed a clear, light brown, sticky gum. Solubility: solvents are the same as for trimethylene phthalate, but hexamethylene phthalate is more soluble.

Anal. after drying to constant weight in high vacuum at 70". Calcd. for $C_{14}H_{16}O_4$: C, 67.75; H, 6.50; molecular weight, 248. Calcd. for $H[O(CH_2)_6OOCC_6H_4CO]_7O(CH_2)_6OH = C_{194}H_{126}O_{30}$: C, 67.35; H, 6.85; molecular weight, 1855. Found: C, 66.74, 66.84; H, 6.75, 6.85; molecular weight by freezing point lowering in benzene, 1700, 1830.

Decamethylene **Phthalate.**—Seven and four-tenths g. of phthalic anhydride and 9 g. of decamethylene glycol were heated at 190–200° for two hours under atmospheric pressure, and at 210–220° for one and one-half hours at 5 mm. The residue was dissolved in benzene, decolorized with Darco and precipitated by petroleum ether. It was a clear, light brown, thick, sticky sirup. Solubility: solvents for decamethylene phthalate are the same as for hexamethylene phthalate, but the former is more soluble.

Anal. after drying to constant weight in high vacuum at 70°. Calcd. for $C_{18}H_{24}O_4$: C, 71.01; H, 7.95; molecular weight, 304. Calcd. for $H[O(CH_2)_{10}OOCC_6H_4CO]_7O(CH_2)_{10}OH = C_{136}H_{190}O_{30}$: C, 70.80; H, 8.39; mol. wt. 2303. Found: C, 70.66, 70.44; H, 8.21, 8.26; molecular weight by freezing point lowering in benzene, 2250, 2060.

Ethylene **Fumarate.**—Fifty-seven and three-tenths g. of diethyl fumarate (0.33 mole) and 25 g. of ethylene glycol (0.4 mole) were heated for ten hours in a stream of nitrogen, the temperature being gradually raised from 190 to 230° and the pressure being reduced at the end to 4 mm. The residue weighed 35 g. or 75% of the calculated amount. It was accompanied by some insoluble material from which it was freed by solution in chloroform, filtration and precipitation with ether. It was washed several times with dry ether. It formed a transparent, slightly yellow, moderately tough mass. After drying it became insoluble in the common solvents.

Anal. after drying to constant weight in high vacuum at 70°. Calcd. for $C_6H_6O_4$: C, 50.70; H, 4.22. Found: C, 51.95, 51.89. H, 6.06, 6.12. Molecular weight determinations could not be made because of the lack of solubility after drying.

Ethylene Maleate.—Thirty-two and five-tenths g. of maleic anhydride (0.33 mole) and 18.6 g. (0.30 mole) of glycol were heated at 195–200° for four hours, and then for some time at 210–215° under reduced pressure. The residue (40 g.) was separated from some insoluble material by solution in warm ethylene chloride and filtration. It was precipitated by cold ether. The product separated as an oil but solidified on standing at 5–10' for two hours. It was a white powder. Most of it melted between 88 and 95°. After drying *in vacuo* it had become insoluble in the common solvents including ethylene chloride and it did not melt below 250°.

Anal. after drying to constant weight in high vacuum at 70°. Calcd. for $C_6H_6O_4$: C, 50.70; H, 4.22. Found: C, 49.87, 49.70; H, 4.36, 4.28. Molecular weight determinations could not be made because of the lack of solubility after drying.

For his kind assistance in the analytical work we here express our thanks to Mr. Wendell H. Taylor.

Summary

The following esters have been prepared: ethylene malonate, ethylene succinate, trimethylene succinate, ethylene adipate, trimethylene adipate, hexamethylene succinate, hexamethylene adipate, ethylene sebacate, trimethylene sebacate, decamethylene succinate, hexamethylene sebacate, decamethylene adipate, decamethylene sebacate, ethylene maleate, ethylene fumarate, ethylene phthalate, trimethylene phthalate, hexamethylene phthalate and decamethylene phthalate. Their molecular weights have been determined. They are all highly polymeric. Their properties are described and their structures are discussed.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SHARP AND DOHME]

A NEW SERIES OF ANESTHETICS. ACYLANILINE DERIVATIVES

BY WALTER H. HARTUNG AND J. C. MUNCH

RECEIVED APRIL 25, 1929 PUBLISHED AUGUST 7, 1929

While working in these Laboratories with m-aminobutyrophenone, it was found that this compound produced anesthesia in the lips and tongue. Examination revealed further that an aqueous solution of its hydrochloride also was anesthetic to the lips and tongue and when injected subcutaneously into animals. This fact was of sufficient interest to warrant investigation of other bases, and their salts, of the same general type as aminobutyrophenone. Accordingly, a series of acylanilines and acyltoluidines was prepared, a series of anesthetics to which no previous reference has been found.

Table I lists those compounds that have been prepared and established by analysis, for only the first two have been previously recorded; the table also includes preliminary data on the toxicity and anesthetic potency of the hydrochlorides as compared to cocaine and novocaine. Other pharmacological studies will be published in an appropriate journal.

Higher homologs have been prepared, but because of the insolubility of their salts in water, due to hydrolysis, they have not been analyzed and, hence, are not included here.

TABLE I

COMPOUNDS AND ACTIVITIES

		M. L. D. of HCl salt mg/kg subcut to guinea pigs	Duration of anesthesia of 1 mg. applied to rabbit cornea, min.
1	m-Aminobutyrophenone	750	20
2	o-Aminobutyrophenone	Over 1000	25
3	m-Aminovalerophenone	Over 1000	25–90
4	(3-Amino-4-methyl-phenyl) ethyl ketone	Over 1000	3
5	(3-Amino-4-methyl-phenyl) propyl ketone	1000	7–14
6	(3-Amino-4-methylphenyl) isopropyl ketone	850	14
7	(3-Amino-4-methylphenyl) *n*-butyl ketone	1000	40
8	(3-Amino-4-methylphenyl) *iso*butyl ketone	500	45
9	Cocaine	60	30
10	Procaine	500	30

It is seen that in order to produce anesthesia at all, the alkyl portion of the ketone must be at least a propyl group, for the ethyl ketone derivative (No. 4) is practically inactive;[1] also, the isopropyl ketone (No. 6) is somewhat less active than the n-propyl compounds (Nos. 1 and 5). The toxicity is surprisingly low. While in the more highly anesthetic compounds the ratio of minimum effective dose to minimum lethal dose is quite high, yet it has been found that a solution of the salts injected subcutaneously into animals is quite irritating, probably because the salts of these aniline derivatives are so highly hydrolyzed in solution and free acid is formed.

Procedure

All of these compounds can be prepared easily, particularly the toluidine derivatives, according to the following scheme

$$\mathrm{ARCOR} \xrightarrow{\mathrm{HNO_3}} \mathrm{AR(NO_2)COR} \xrightarrow{\mathrm{H_2}} \mathrm{AR(NH_2)COR}$$

The mixed arylalkyl ketones were prepared from the appropriate acid chloride and benzene or toluene by the Friedel–Crafts reaction. All the ketones used here are described in Beilstein.

The nitro compounds were obtained by adding the ketones slowly to cold agitated fuming nitric acid in the ratio of 75 cc. of acid to a tenth mole of ketone, the temperature being kept below +10°. Fuming nitric acid was found most satisfactory in nitrating butyrophenone; it was also discovered that if most of the fumes were first removed by bubbling air through the acid, the nitration of butyrophenone went more smoothly

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[1] This compound produces no anesthesia when injected subcutaneously in dogs.

and to greater extent. Hence for all subsequent nitrations fuming acid from which most of the fumes had been expelled was used. After complete addition of the ketone the mixture was allowed to stand in the ice-bath for another minute and then poured into excess ice water. In cases where the resulting nitro ketone was a solid, it was filtered off, washed and recrystallized from an appropriate medium; when liquid, it was quickly drawn off in a separatory funnel, washed with bicarbonate solution to remove adhering acid, dried and distilled. The yields varied from 60 to 80%.

The position taken by the entering nitro group was proved by oxidation to the aromatic acid, which was then identified.

The reduction proceeded very smoothly by dissolving the nitro ketone in an equal weight of acetic acid, adding an equal weight of mossy tin, warming and slowly adding sufficient concentrated hydrochloric acid to dissolve all of the metal. The amine was isolated by adding excess alkali, extracting with ether, drying and distilling. The yield of the amine was from 60 to 80% based on the nitro compound.

The hydrochloride salts were prepared by adding to an ethereal solution of the free base an absolute alcoholic solution of hydrogen chloride. The salt usually came down immediately and could be recrystallized from a concentrated solution in absolute alcohol; the mother liquors, however, retained the greater part of the salt in solution; it could be forced out by dilution with ether.

Experimental

***m*-Aminobutyrophenone and o-aminobutyrophenone,** with their corresponding intermediates, have been described by Morgan and Hickenbottom.[2]

Table II contains a tabular summary of the data concerning the other intermediate nitro compounds, and in some cases their semicarbazones.

TABLE II

NITRO COMPOUNDS

Ketone	Recryst. from	M. p. or b. p., °C.
m-Nitrovalerophenone	Liquid	145–150 (3 mm.)
(3-Nitro-4-methylphenyl) ethyl[a]	Dil. alc.	51
(3-Nitro-4-methylphenyl) propyl	Toluene	77.5
(3-Nitro-4-methylphenyl) isopropyl	Ligroin	41.0
(3-Nitro-4-methylphenyl) n-butyl	Ligroin	48.0
(3-Nitro-4-methylphenyl) *iso*butyl	Ligroin	54.5

The nitro ketones were oxidized with dilute nitric acid and in each case gave *m*-nitrobenzoic acid or the *p*-methyl-*m*-nitrobenzoic acid.

[a] This compound is described in Beilstein, 4th ed., Vol. VII, p. 318.

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[2] Morgan and Hickenbottom, J. Chem. *Soc.*, 119, 1879 (1921).

TABLE II (*Concluded*)

	Nitrogen analyses (Kjeldahl)		Semicarbazone			
					Nitrogen analyses[a]	
Formula	Calcd., %	Found, %	M. p., °C.	Formula	Calcd., %	Found, %
$C_{11}H_{13}O_3N$	6.76	6.48 6.55 6.80	...	....	...	...
......	..	....	...	....	...	...
$C_{11}H_{13}O_3N$	6.76	6.51 6.92	215–216	$C_{12}H_{16}O_3N_4$	10.60	10.14 11.06
$C_{11}H_{13}O_3N$	6.76	6.74 6.87	...	....	...	...
$C_{12}H_{15}O_3N$	6.34	6.16 6.36	210	$C_{13}H_{18}O_3N_4$	10.07	10.08
$C_{12}H_{15}O_3N$	6.34	6.32 6.18	214	$C_{13}H_{18}O_3N_4$	10.07	10.24

[a] The available nitrogen was determined according to the method of Rimini (*Z. anal. Chem.*, **47,645 (1908)).**

Table III gives in tabular form the data for the amino compounds and those derivatives that have been prepared.

TABLE III

DATA ON AMINO COMPOUNDS

Ketone, ( ) = (3-amino-4-methylphenyl)	Free base		Acetamino deriv.	Hydrochloride
	B. p., °C.	M. p., °C.	M. p., °C.	M. p., °C.
1 m-Aminovalerophenone	**160–163 (3** mm.)	Liquid	[a]	**155** 5–156.0[b]
2 ( ) ethyl	**190–195** (20 mm.)	85.5–86.0[c]	**131.5**[c,d]	**204** (dec.)
3 ( ) propyl	150–165 **(3 mm.)**	**69.**0[c]	130.5	168
4 ( ) isopropyl	**150–153 (3** mm.)	Liquid	...	167.5[e]
5 ( ) n-butyl	170–185 (3 mm.)	61.0[f]	**93–94'**	**91.5–93.**0[h]
6 ( ) *iso*butyl	165–170 **(3** mm.)	Liquid	**117.5'**	142.5'

[a] The acetyl derivative of m-aminovalerophenone was not analyzed as such; however, with permanganate it was oxidized to an acid which melted at **237°,** identified **as** m-acetaminobenzoic acid. [b] This salt is purified with difficulty. **It** hydrolyzed almost completely in water and was best recrystallized from anhydrous *iso*propyl alcohol. [c] Recrystallized from toluene. [d] Formed a semicarbazone (not analyzed) which melted with decomposition at **203.5'.** [e] Prepared by adding an absolute alcoholic solution of hydrogen chloride to an absolute ethereal solution of the free base. The salt could be recrystallized from anhydrous isopropyl alcohol or **from** toluene. [f] Recrystallized from **ligroin.** Recrystallized from **benzene–ligroin** mixture (1:2). Recrystallized from xylene. The salt is not so well defined **as** its lower homologs. Chlorine and nitrogen determinations were unsatisfactory. It did not dissolve completely in water **without** further addition of acid. [i] Dissolves in water with slight turbidity.

NITROGEN ANALYSES (KJELDAHL) OF FREE BASE AND ACETAMINO DERIVATIVE

	Free base			Acetamino derivative		
	Formula	Calcd., %	Found, %	Formula	Calcd., %	Found, %
1	$C_{11}H_{15}ON$	..	..	....	..	..
2	$C_{10}H_{13}ON$	8.59	8.75	$C_{12}H_{15}O_2N$	6.83	6.58
3	$C_{11}H_{15}ON$	7.90	7.90	$C_{13}H_{17}O_2N$	6.39	6.53 6.41
4	$C_{11}H_{15}ON$	7.90	7.78 7.77	....	..	..
5	$C_{12}H_{17}ON$	7.33	7.31 6.91	$C_{14}H_{19}O_2N$	6.00	5.83
6	$C_{12}H_{17}ON$	7.33	7.24 7.42	$C_{14}H_{19}O_2N$	6.00	5.87

TABLE III (*Concluded*)

ANALYSES OF HYDROCHLORIDE

	Formula	Chlorine (as AgCl) Calcd., %	Chlorine (as AgCl) Found, %	Nitrogen (Kjeldahl) Calcd., %	Nitrogen (Kjeldahl) Found, %
1	$C_{11}H_{15}ON \cdot HCl$	16.60	16.15 16.20	6.57	6.71
2	$C_{10}H_{13}ON \cdot HCl$	17.76	17.43 17.42	7.01	6.73 6.72
3	$C_{11}H_{15}ON \cdot HCl$	16.60	16.63 16.67	..	..
4	$C_{11}H_{15}ON \cdot HCl$	16.60	16.55 16.37	..	..
5	$C_{12}H_{17}ON \cdot HCl$	...	[a]	..	..
6	$C_{12}H_{17}ON \cdot HCl$	15.58	15.05 15.37	..	..

[a] Chlorine and nitrogen determinations were unsatisfactory.

Summary

1. Acylanilines and acyltoluidines have anesthetic properties, particularly their hydrochlorides, if there is at least a butyrophenone skeleton.
2. Data concerning eight such compounds are given.
3. Six of the eight amines are new and are described together with their intermediates and, in some cases, their derivatives.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. I. REDUCTION PRODUCTS OF ROTENONE

BY F. B. LAFORGE AND L. E. SMITH

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Rotenone, the active insecticidal principle of Derris *elliptica*, has been the subject of numerous investigations in recent years.[1] As it is perhaps natural to expect in the case of such a complicated compound, the published chemical articles contain numerous errors, corrections and retractions. It is indeed only in the past year that the empirical formula of rotenone has been established with certainty.

A large share of what is known of the chemistry of the compound has been contributed by the Japanese. Nagai[2] seems to have been the first to isolate it in a pure state. He gave it its present name and showed that it contained a keto group. Ishikawa[3] found that the compound was optically active, and Kariyone[4] showed the presence of methoxyl and an unsaturated bond, and obtained tubaic acid of the formula $C_{12}H_{12}O_4$

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[1] The Insecticide Division of the Bureau of Chemistry and Soils has collected and abstracted over 250 articles on *Derris,* and a publication entitled "A Bibliography of *Derris (Deguelia)* Species Used as Insecticides," by Dr. R. C. Roark, will be issued shortly in multigraphed form.

[2] Nagai, *J. Tokyo Chem. Soc.,* 23, 740 (1902).

[3] Ishikawa, *Tokyo Medical J.,* 31, No. 4 (1917).

[4] Kariyone and Atsumi, *J. Pharm. Soc.* (Japan), No. 491, 10 (1923); Kariyone, Kimura and Kondo, *ibid.,* No, 514, 1049 (1924); Kariyone and Kondo, *ibid.,* No. 518, 376 (1925).

by fusion with potassium hydroxide. Takei[5] in his first article added some facts to those found by the other Japanese investigators, but most of his results were reinterpreted in another publication[6] in which he finally decided upon the empirical formula $C_{23}H_{22}O_6$, which brought it into agreement with the figures obtained by him and others with respect to the methoxyl content and the analytical figures obtained for the phenylhydrazone, various empirical formulas having been proposed by previous investigators.

Butenandt[7] repeated some of the work of the Japanese chemists and established with certainty the empirical formula finally decided upon by Takei. He also prepared a number of new and important derivatives, but the facts so far obtained are insufficient to establish its constitution.

The investigations which will be described in this article deal principally with results obtained by the direct hydrogenation of rotenone and by the action of metallic zinc in alkaline alcoholic solution.

The simplest reduction product of rotenone, dihydrorotenone, was prepared by Kariyone by hydrogenation with palladium–barium sulfate catalyst and is described as prisms, melting at 216°, $[\alpha]_D^{20}$ $-222°$, yielding an oxime of melting point 258°.

Butenandt repeated the preparation of dihydrorotenone, according to the directions of Kariyone, confirmed the results of the Japanese investigator with respect to its physical properties and revised the formula to $C_{23}H_{24}O_6$. He employed dihydrorotenone for subsequent reactions to test a theory regarding the formation of his "derritol."

We have made a large number of experiments on the hydrogenation of rotenone with both palladium–barium sulfate and platinum oxide catalysts in acetone and acetic ester solutions, but our results differ widely from those reported by Kariyone and Butenandt.

With the first-mentioned catalyst in acetone solution, absorption of hydrogen takes place until about 56 cc. per gram of rotenone is consumed, when the reaction practically stops. With platinum catalyst, it proceeds rapidly to about the same point, but continues at a much slower rate without any definite end-point. In both cases two compounds are formed, if the reaction is discontinued after about one molecule of hydrogen has been absorbed. Since one product is an acid and the other a neutral compound, the two are easily separated by agitating the ethereal solution of the mixture with dilute sodium hydroxide solution. The acid is precipitated in crystalline form from the alkaline solution by the addition of mineral acid, whereas the neutral compound crystallizes on evaporation of the ethereal solution. Both are easily purified, the

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[5] Takei, *Biochem. Z.*, 157, 1 (1925).

[6] Takei, Ber., 61, 1003 (1928).

[7] Butenandt, Ann., 464, 253 (1928).

acid by crystallization from dilute alcohol, and the neutral compound from 95% alcohol. The combined yields of the two are about equal to the quantity of rotenone reduced. The acid crystallizes in needles and melts at 209°, the neutral substance in prisms melting at 164°. Both have the same empirical formula, $C_{23}H_{24}O_6$.

The optical rotation of the neutral compound was found to be $(\alpha)_D^{20} = 225''$. It yielded an oxime melting at 258°, the same compound that was obtained by hydrogenation of rotenone oxime. There seems to be no doubt that the neutral compound is dihydrorotenone, and except for the melting point, where we have noted a very great discrepancy, our results are in agreement with those found by Kariyone.

Both the acid and dihydrorotenone are capable of further reduction. On long continued reduction with platinum catalyst in acetic ester solution, the acid takes up another molecule of hydrogen, yielding a new acid of the formula $C_{23}H_{26}O_6$, melting point 215°.

Dihydrorotenone is more slowly reduced under the same conditions, and yields as one of the end-products the same acid as does the original acid product, perhaps together with some of the dihydrodesoxyrotenone of Butenandt, in which the keto group is reduced.

From these results, it is apparent that the rotenone molecule is simultaneously attacked in two places on catalytic reduction. One reaction probably involves the simple reduction of an unsaturated bond, yielding dihydrorotenone, the other, the opening of a lactone linkage to form an acid which still contains the original double bond of rotenone. Further reduction of either compound then leads to the same end-product, an acid containing four hydrogen atoms more than rotenone.

Butenandt obtained an acid $C_{23}H_{26}O_6$, melting point 206°, by the reduction of rotenone with platinum catalyst in saturated alcoholic ammonia, which may be identical with the acid described above of the same formula.

The isorotenone described by Takei does not absorb hydrogen as does rotenone, and it seems likely that it contains no unsaturated bond, but a ring structure instead.

Among the derivatives prepared by Butenandt is a phenolic compound of a bright yellow color, containing the original keto group, but possessing two carbon atoms less than rotenone, and named by him "derritol." It is formed with a compound called rotenol in which the keto group is probably reduced to an alcoholic group. These compounds result from the reduction of rotenone with zinc dust in alkaline alcoholic solution.

We have found that by slight modification of this method, either of these compounds may be made the predominating product. Two or more by-products of lower molecular weight are formed in this reaction, and have been isolated in crystalline form.

According to Butenandt's theory, the presence of a double bond is essential to the formation of derritol, since he was unable to obtain a corresponding compound from dihydrorotenone. It seems doubtful, however, that Butenandt was working with dihydrorotenone, for this compound readily gives a derivative of the formula of dihydroderritol as well as dihydrorotenol, when subjected to the alkaline zinc reduction process. The first-mentioned compound is, however, colorless instead of yellow, but it gives the same phenol reaction with ferric chloride as does derritol. Isorotenone, which probably contains no double bond, is also readily converted into isoderritol and isorotenol by reduction with zinc in alkaline solution. It seems probable, therefore, that whatever the mechanism of the reaction leading to the formation of derritol may be, it is not dependent upon the presence of a double bond.

Rotenone.—The preparation of rotenone is so simple as to require no detailed description. Three or four extractions of the coarsely ground, dried root with ether is sufficient to dissolve out all the rotenone, which crystallizes in nearly pure state from the concentrated extract. It is recrystallized from about 20 parts of boiling absolute alcohol. Crystallization takes place so rapidly on cooling that it is necessary to filter on a hot funnel. A little decolorizing carbon is used to obtain a pure white product. Rotenone melts at 163°. The yield of pure product varies with the quality of the *Derris* root. A fairly good material yields 2.5% of recrystallized rotenone, although we have analyzed samples containing less than 0.5%, while some Japanese chemists claim a yield of more than 6%.

Dihydrorotenone.[4,7]**—Four** grams of rotenone was added to 30 cc. of acetic ester containing about 0.3 g. of platinum oxide catalyst[8] previously saturated with hydrogen, and the solution was shaken in a hydrogen atmosphere. About 250 cc. is absorbed in three or four minutes, but if sufficient time is allowed, 400 cc. or more will be taken up. The reduction in this case, however, was discontinued after the absorption of about one equivalent of hydrogen. The solution was poured off from the catalyst, diluted with 100 cc. of ether and extracted several times with 5% aqueous potassium hydroxide.

The ether acetic ester solution was dried and evaporated to a colorless sirup which readily crystallized on cooling. The crystalline cake was rubbed up with a few cubic centimeters of alcohol, filtered and dried. The yield was in one experiment 1.9 g.; in another carried out under the same conditions, 1.7 g. The material is easily recrystallized from 95% alcohol, from which it is deposited in prisms often 1 mm. or more in length. The loss on recrystallization is small, and hence the compound is easily purified. After one recrystallization the compound melts at 164°, and further recrystallization does not alter the melting point. The analytical figures agree for the expected formula for dihydrorotenone.

Anal.[9] Subs., 0.0893, 0.0820, 0.0821: CO_2, 0.2285, 0.2100, 0.2107; H_2O, 0.0490,

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[8] R. Adams and R. L. Shriner, THIS JOURNAL, 45, 2171 (1923).

[9] It is necessary to mix the substance with copper oxide in order to obtain satisfactory results.

0.0448, 0.0465. Subs., 0.0228, 0.0260: AgI, 0.0265, 0.0313. Calcd. for $C_{23}H_{24}O_6$: C, 69.69; H, 6.06; $2OCH_3$, 15.65. Found: C, 69.77, 69.82, 69.98; H, 6.09, 6.07, 6.28; OCH_3, 15.27, 15.90. 0.3153 g. of subs. in 15 *cc.* of benzene rotated in a 2-dm. tube −9.46°; $[\alpha]^{20}_D$ = −225.2'.

Acid Reduction Product.—The aqueous alkaline extract from the reduction mixture yields a crystalline product on the addition of an excess of hydrochloric acid. The compound is best purified by dissolving in hot alcohol and adding an equal volume of hot water to the solution. The compound crystallizes in needles which melt at 209°.

If the reduction has been carried too far, a mixture of two acids is obtained, which will be referred to later.

The yield is, as in the first case described, 1.7 g., and 1.9 g. in the second. In another experiment, in which 6 g. of rotenone was reduced, 3 g. of acid was obtained, together with 2 g. of pure dihydrorotenone. Similar results were obtained in a number of other runs. The compound may be titrated but the end-point is not sharp.

Anal. Subs, 0.0833, 0.0828, 0.0805: CO_2, 0.2124, 0.2106, 0.02045; H_2O, 0.0462, 0.0446, 0.0455. Subs., 0.0222, 0.0182: AgI, 0.0264, 0.0218. Calcd. for $C_{23}H_{24}O_6$: C, 69.69; H, 6.06; $2OCH_3$, 15.65. Found: C, 69.55, 69.36; 69.28; H, 6.16, 5.99, 6.27; OCH_3, 15.71, 15.82. 0.3154 g. of subs. in 15 cc. of chloroform rotated in a I-dm. tube +0.76°; $[\alpha]^{20}_D$ = $36.2"; 0.0562 subs. = 1.24 cc. of $N/10$ acid; *M,* calcd., 396; found, 453.

Reduction of Rotenone **with** Palladium–Barium Sulfate Catalyst.—One and a half grams of rotenone was reduced in acetone solution with 0.5 g. of palladium–barium sulfate catalyst, according to the directions of Butenandt and Kariyone.

The absorption of hydrogen ceased in about thirty minutes, when 84 cc. had been taken up. This volume of hydrogen corresponds to the theoretical quantity for two atoms per molecule of rotenone. The solvent was evaporated and the residue dissolved in ether, and the two resulting compounds were separated in the manner described above. With palladium–barium sulfate catalyst the dihydrorotenone predominates in the mixture, 1.04 g. being isolated. The same acid was formed as in the cases where platinum was used, the yield amounting to 0.45 g. In another experiment in which 2 g. of rotenone was employed, 1.5 g. of dihydrorotenone was obtained.

Reduction of Dihydrorotenone.—One gram of dihydrorotenone was subjected to long-continued hydrogenation with 0.2 g. of platinum oxide catalyst in acetic ester solution. After about three hours, 20 cc. of hydrogen had been absorbed and the product was worked up as in previous cases. The ethereal solution of the reaction products was extracted with dilute potassium hydroxide, and on acidification yielded 0.08 g. of acid. It was recrystallized from 50% acetic acid. The product crystallizes in needles melting at 215°.

Anal. Subs., 0.0728: CO_2, 0.1854; H_2O, 0.0436. Calcd. for $C_{23}H_{26}O_6$: C, 69.30; H, 6.58. Found: C, 69.44; H, 6.65.

The neutral reduction product was probably mostly dihydrorotenone, but may have contained the dihydrodesoxyrotenone of Butenandt.

Reduction of the Acid Reduction Product of Rotenone.—One-half gram of the acid product described above, as obtained by reduction of rotenone, was subjected to a second reduction with platinum catalyst in acetic ester solution. About 36 cc. of hydrogen was taken up in fifteen minutes. The solution was evaporated and the crystalline product recrystallized from hot 50% alcohol. It crystallized in needles which melted at 215'. A mixture of this product and the acid obtained from dihydrorotenone melted also at 215°.

Anak. Subs., 0.0903: CO_2, 0.2285; H_2O, 0.0524. Calcd. for $C_{23}H_{26}O_6$: C, 69.30; H, 6.58. Found: C, 69.00; H, 6.46.

Apparently the two acids obtained—the one from dihydrorotenone and the other from the first acid reduction product—are identical.

If rotenone is allowed to absorb more than two atoms of hydrogen, a mixture of the partly and fully hydrogenated acids is obtained.

Oxime of Dihydrorotenone.—The oxime of dihydrorotenone is readily obtained either by hydrogenation of rotenone oxime[6] or by the action of hydroxylamine on dihydrorotenone.

Two grams of rotenone oxime in 50 cc. of acetone containing 0.4 g. of platinum catalyst, which had been saturated with hydrogen, absorbed 120 cc. of hydrogen in three to four minutes. The solvent was evaporated and the product recrystallized from absolute alcohol, in which it is difficultly soluble. It crystallizes in long needles and melts with decomposition at 256–257°. The yield is quantitative.

The same compound is also obtained when 1.6 g. of dihydrorotenone, 1.1 g. of hydroxylamine hydrochloride, 1.2 g. of anhydrous sodium acetate and a few drops of acetic acid in 20 cc. of absolute alcohol are boiled for from four to five hours under reflux. The oxime crystallized out on cooling and was recrystallized from absolute alcohol. The yield was 1.2 g. of product, melting at 256° with decomposition. A mixed melting point of the compound with that obtained by reduction of rotenone oxime showed no depression.

Kariyone also records 256° as the melting point of dihydrorotenone oxime.

Anal. Subs., 0.0948: CO_2, 0.2325; H_2O, 0.0512. Subs., 0.0212, 0.0229: AgI, 0.0249, 0.0264. Calcd. for $C_{23}H_{25}O_6N$: C, 67.15; H, 6.08; $2OCH_3$, 15.09. Found: C, 66.88; H, 6.00; OCH_3, 15.50, 15.24.

Benzenesulfonic Acid Derivative of Rotenone **Oxime.**—Five grams of rotenone oxime prepared by the directions of Takei was dissolved in 20 cc. of dry pyridine and 2 g. of benzenesulfonic acid chloride was slowly added. After about eighteen hours, the solution was poured into 100 cc. of 5% sulfuric acid. The amorphous precipitate crystallized in a few minutes. It was washed with water and recrystallized by dissolving in 30 cc. of hot alcohol and adding 15 cc. of hot water. It was again recrystallized from 90% alcohol and yielded 4 g. of white needles, melting at 143°.

Anal. Subs., 0.0242: AgI, 0.0212. Subs., 0.0225, 0.0230: 1.22, 1.22 cc. of $N/30$ HCl. Subs., 0.1481: $BaSO_4$, 0.0576. Calcd. for $C_{29}H_{26}O_8SN$: $2OCH_3$, 11.29; N, 2.55; S, 5.82. Found: OCH_3, 11.57; N, 2.53, 2.48; S, 5.34.

Numerous attempts were made to effect the Beckmann rearrangement on the compound, without success. Both alkaline and acid reagents decompose the compound in such a manner as to yield only tarry products from which nothing definite could be isolated.

Dihydrorotenone **Iso-oxime.**—Dihydrorotenone oxime is apparently converted into an isomeric compound by the action of concentrated hydrochloric acid. One gram was allowed to stand in contact with 15 cc. of concentrated hydrochloric acid for three days. It turned yellow, but the color disappeared on dilution with water. The product was recrystallized from absolute alcohol and formed long needles, melting at 270 to 273" with decomposition. The yield was quantitative.

Anal. Subs., 0.0999: CO_2, 0.2453; H_2O, 0.0537. Subs., 0.0225, 0.0208: AgI, 0.0252, 0.0243. Calcd. for $C_{23}H_{25}O_6N$: C, 67.15; H, 6.08; $2OCH_3$, 15.09. Found: C, 66.96; H, 5.96; OCH_3, 14.80, 15.44.

Preparation of Rotenol and **Derritol.**—In following the directions of Butenandt[7] for the preparation of these derivatives, it was found that while the yield of rotenol was fairly good, the product obtained from the alkaline extract was very difficult to crystallize and the yield of derritol very unsatisfactory. However, if the alcoholic potassium hydroxide solution containing the rotenone was first heated nearly to boiling, and the zinc dust was added subsequently, the yield of derritol was greatly improved. It was also found that by varying the percentage of potassium hydroxide, the quantities of both rotenol and derritol obtained could be varied at will.

Below are listed some typical runs, 3 g. of rotenone being used in each case.

Potassium hydroxide, %	5	10	15	20
Rotenol, grams	2.0	1.1	0.9	C.2
Derritol, grams	0.1	0.65	0.95	1 15

If larger quantities of rotenone were employed, mechanical stirring was necessary to obtain corresponding yields. The melting point of pure derritol was found to be 164°, instead of 161" as recorded by Butenandt, and rotenol melted sharply at 120° instead of 115°. The optical rotation of derritol was measured, with the following result: 0.1700 g. of substance in 5 cc. of $CHCl_3$ rotated in 1-dm. tube −2.25"; $[\alpha]^{20}_D = -66.2°$.

On concentrating the derritol mother liquors, a small quantity of another crystalline substance melting at 161° was obtained. The methoxyl content of this substance was about 1% higher than that of derritol.

Anal. Subs., 0.0207, 0.0213: AgI, 0.0279, 0.0283. Found: CH_3O, 17.80, 17.55

Since the yield was small, no further work was done on this compound.

The mother liquors of rotenol contain traces of an oil with a terpene-like odor; this oil is volatile with steam and can be isolated from the distillate by ether extraction. It has not yet been identified.

Preparation of Dihydrorotenol and **Dihydroderritol.**—The dihydrorotenol and dihydroderritol were prepared in the same manner as described for the preparation of rotenol and derritol. With 15% potassium hydroxide and 3 g. of dihydrorotenone, the yield of the alkali-insolublecompound (dihydrorotenol) was 0.8 g. It was recrystallized from methyl alcohol and melted at 131°. This is in agreement with the melting point of dihydrorotenol obtained by Butenandt. The yield of the alkali-soluble fraction was 0.5 g. Recrystallized from dilute methyl alcohol, it formed white needles, melting at 122°. It gives a strong color test for phenol with ferric chloride and the analysis indicates that it is dihydroderritol.

Anal. Subs., 0.0635, 0.0623: CO_2, 0.1576, 0.1550; H_2O, 0.0360, 0.0365. Subs., 0.0233: AgI, 0.0295. Calcd. for $C_{21}H_{24}O_6$: C, 67.74; H, 6.45; $2OCH_3$, 16.66. 'Found: C, 67.68, 67.84; H, 6.30, 6.51; OCH_3, 16.72.

Preparation of Isorotenol and **Isoderritol.**—The isorotenone used in the preparation of isorotenol and isoderritol was prepared by the method of Takei.[6] The product so obtained had a melting point of 184°. This figure is about 7° higher than that recorded by Takei, but confirms the figure found by Wright.[10] However, since the analytical data of both Takei and Wright for carbon and hydrogen were at some variance from the theoretical, the carbon and hydrogen determination was repeated on our product.

Anal. Subs., 0.0907, 0.0906: CO_2, 0.2324, 0.2320; H_2O, 0.0460, 0.0447. Calcd. for $C_{23}H_{22}O_6$: C, 70.05; H, 5.59. Found: C, 69.88; 69.84; H, 5.63, 5.48.

Isorotenone was treated with 15% potassium hydroxide and zinc in the same manner that has been described for the preparation of rotenol and derritol. From 3.0 g. of isorotenone, 0.9 g. of the product (isorotenol) insoluble in alkali was obtained. It crystallized from methyl alcohol in white needles, melting at 133°.

Anal. Subs., 0.0653, 0.0670: CO_2, 0.1611, 0.1711; H_2O, 0.0371, 0.0363. Subs., 0.0202: AgI, 0.0240. Calcd. for $C_{23}H_{24}O_6$: C, 69.67; H, 6.10, $2OCH_3$, 15.65. Found: C, 69.35, 69.63; H, 6.31, 6.03; OCH_3, 15.69.

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[10] Wright, THIS JOURNAL, 50,3355 (1928).

The alkali-soluble portion gave 0.9 g. of a compound (isoderritol) which crystallized from methyl alcohol in light yellow plates, melting at 150°.

Anal. Subs., 0.0728, 0.0773: CO_2, 0.1814, 0.1925; H_2O, 0.0381, 0.0409. Subs., 0.0209: AgI, 0.0268. Calcd. for $C_{21}H_{22}O_6$: C, 68.07: H, 5.99; $2OCH_3$, 16.75. Found: C, 67.93, 68.00; H, 5.81, 5.88; OCH_3, 16.93.

Summary

Hydrogenation of rotenone results in the formation of a neutral and an acid compound as primary products.

The neutral compound is dihydrorotenone and is formed by the simple reduction of an unsaturated bond. Dihydrorotenone melts at 164°, instead of 216° as recorded by Kariyone.

The acid is easily separated from the reaction mixture and has the same empirical formula as dihydrorotenone, $C_{23}H_{24}O_6$.

On further reduction, both compounds yield the same end-product, an acid containing four more hydrogen atoms than rotenone. It seems likely that the molecule of rotenone is first simultaneously reduced in two places, while further hydrogenation results in the acid, $C_{23}H_{26}O_6$.

Contrary to Butenandt, dihydrorotenone is converted into dihydroderritol and dihydrorotenol by treatment with zinc in alkaline alcoholic solution.

Isorotenone yields isoderritol and isorotenol by the same treatment.

From these results, it follows that the formation of derritol is independent of the presence of an unsaturated bond in rotenone.

The preparation and properties of some other rotenone derivatives are described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY]

SYNTHESIS IN THE DIPHENYL ETHER SERIES. I. PREPARATION OF SOME SIMPLE DERIVATIVES[1]

BY C. M. SUTER

RECEIVED MAY 2, 1929 PUBLISHED AUGUST 7, 1929

Since diphenyl ether is now readily available, a further study of its derivatives and their preparation from the parent substance seems desirable. Most of such derivatives previously prepared have been made by the reaction between the salt of a phenol and an aromatic halogen compound.[2]

The preparation of o- and *p*-nitrodiphenyl ether by the nitration of

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[1] Presented before the Division of Organic Chemistry at the Columbus meeting of the American Chemical Society, May, 1929.

[2] See Raiford and Colbert, THIS JOURNAL, 48, 2652 (1926), for recent work and bibliography.

diphenyl ether has been investigated by Mailhe and Murat,[3] who used fuming nitric acid in acetic acid solution. They claimed complete separation of the two isomers by freezing out the para derivative. No yields were reported. The *p*-nitro isomer was also obtained by Ryan and Drumm[4] in their nitration of diphenyl ether with nitrogen oxides or nitric acid, but no satisfactory method of preparation was indicated.

The method of Mailhe and Murat was found to be unsatisfactory because of the formation of alkali-soluble products and the necessity of using a large excess of nitric acid. Addition of sulfuric acid to the nitrating mixture increased the formation of tar. A very suitable method was found in the use of acetic anhydride as a solvent for the diphenyl ether, the nitric acid being added in acetic acid solution. This method was studied in detail to find the optimum conditions for a high yield of the mononitro derivatives. A table of results and details of the method are given in the experimental part.

The ortho and para isomers are not readily separable by fractional distillation as their boiling points at 20 mm. are only 4° apart. The para isomer is only partially separated by cooling to 0°, the remaining oil containing about 25% of this product. Since the amines obtained by reduction of this mixture are easily separated by the difference in solubilities of their sulfates, further purification of the nitro compounds was not attempted.

The corresponding nitriles were prepared from the two amines. These upon hydrolysis gave the acids which have been previously prepared by other methods.[5]

The bromination of diphenyl ether has been previously studied by Mailhe and Murat,[6] who reported a mixture of bromo and dibromo derivatives in which the bromine entered only the para positions. The structure of these compounds was proved by Le Fèvre and co-workers.? Repetition of the bromination using equimolecular quantities of bromine and the ether gave only 47% of *p*-bromodiphenyl ether, the rest of the bromine forming the dibromo derivative and a trace of higher brominated product. The large amount of dibromo compound formed indicates that the presence of a bromine atom in one ring inhibits only slightly the entrance of a second bromine atom in the other ring. This is in contrast to the influence of the nitro group, since in nitration of diphenyl ether it is possible to obtain a high yield of mononitro derivatives with the formation of comparatively little dinitro compounds.

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[3] Mailhe and Murat, *Compt. rend.*, 154, 715 (1912).

[4] Ryan and Drumm, *Sci. Proc. Roy. Dublin Soc.*, 17, 313 (1924); C. *A.*, 18, 1655 (1924).

[5] Ullmann and Zlokasoff, *Ber.*, 38,2112 (1905); Griess, *ibid.*, 21,980 (1888).

[6] Mailhe and Murat, *Compt. rend.*, 154, 601 (1912).

[7] Le Fèvre, Saunders and Turner, J. *Chem. Soc.*, 1168 (1927).

Bromination of the *p*-nitro- and p-acetaminodiphenyl ethers gave only the compounds containing the bromine in the second para position, indicating that in general in diphenyl ether derivatives the tendency for bromine to enter the ortho position is small.

Experimental

Nitration of Diphenyl Ether.—Best results were obtained as follows. A solution of 100 cc. (2.4 moles) of fuming nitric acid (sp. gr 1.52) in 300 cc. of glacial acetic acid was added over a period of two hours to a well-stirred solution of 340 g. (2 moles) of diphenyl ether in 400 cc. of acetic anhydride kept in a water-bath at a temperature of 25–30°. After three and a half hours longer the reaction mixture was poured into water, the precipitated oil washed twice and distilled under reduced pressure. The mononitro compounds came over at 193–210° (uncorr.) at 14 mm., a mixture of 50 *g.* of dinitro isomers remaining in the distilling flask; yield, 370 g or 86% of the theoretical.

From 700 g. of the mononitro mixture kept at 0° overnight was obtained 270 g. of practically pure *p*-nitrodiphenyl ether by filtering and washing the crystals with methyl alcohol. Since reduction indicated about 25% of para isomer in the remaining oil, 54% of the original mixture was the para derivative. After two crystallizations from the same solvent the melting point was 57°; reported, 56, 60–61°.

The effect of various changes in the above method of nitration upon the yield obtained is indicated in Table I.

TABLE I

CONDITIONS AND YIELDS

$(C_6H_5)_2O$, moles	$(C_6H_5)_2O$ solvent, *cc.*	HNO_3, moles	HNO_3 solvent, *cc.*	Nitro, %	Dinitro, %	$(C_6H_5)_2O$ recovered, %
0 5	AcOH, 200	2.5	None	26	Trace	42
.5	AcOH, 75	1.5	AcOH, 100	36	Trace	14 (0.5 mole H_2SO_4)
.5	Ac_2O, 100	0.75	Ac_2O, 100	82	10	Trace
.5	Ac_2O, 100	1.0	Ac_2O, 100	62	33	None
.5	Ac_2O, 100	2.5	Ac_2O, 100	Trace	106	None (some trinitro?)
2.0	Ac_2O, 400	2.0	AcOH, 300	71	5	15
2.0	Ac_2O, 400	2.4	AcOH, 300	86	10	2
2.0	Ac_2O, 400	2.7	AcOH, 300	78	18	None
2.0	Ac_2O, 300	2.4	AcOH, 300	77	8	13
2.0	Ac_2O, 400	3.0	AcOH, 400	78	15	None

The first two reactions were run at 45–50', the others at 25–30°. In the reactions involving 2 moles of the ether the time of the reaction was five hours and twenty minutes. In the others it was about three hours.

***p*-Aminodiphenyl** Ether.—This was prepared by two methods: reduction of the nitro compound with iron powder and hydrochloric acid, or by the use of zinc and calcium chloride in a water–alcohol mixture. The latter gave the better results. To a well stirred mixture of 80 g. of zinc dust and 20 g. of calcium chloride in 75 cc. of water and 200 cc. of 95% alcohol on a steam-bath was added slowly **43** g. (0.2 mole) of the nitro compound. The reaction was very vigorous. After an hour the mixture was filtered to remove zinc oxide and unchanged zinc. The filtrate upon cooling deposited a few crystals of the hydrazo compound. These were removed and the solution diluted with water, which gave a light yellow mass of the amine; yield, 37 g., theoretical amount of crude product; m. p. 75–80"; reported m. p. 83.5° for the pure amine.[8] The crude product was readily purified by distillation, b. p. 187–189" (corr.) at 14 mm.

o-Aminodiphenyl Ether.—This was prepared similarly to the method given for the para isomer by reducing the mixture of nitro compounds, dissolving the mixed amines in hydrochloric acid and precipitating the *p*-amine as the sulfate, which is practically insoluble in cold water.[9] The yield in a typical run was 54% of ortho and 21% of para derivative. The o-amine distilled at 172–173° (corr.) at 14 mm., m. p. 44-45'; previously reported, 44°.[10]

The acetyl derivative solidified only after standing for several days. Recrystallized from dilute methyl alcohol, the melting point was 81°.

Anal. Calcd. for $C_{14}H_{13}O_2N$: N, 6.17. Found: N, 6.02, 6.16.

***p*-Cyanodiphenyl** Ether.—Thirty-seven grams of finely-divided p-aminodiphenyl ether was warmed on a steam-bath with 60 cc. of concentrated hydrochloric acid and 150 cc. of water. The suspension of amine hydrochloride was cooled to 0° and diazotized with 15 g. of sodium nitrite in 40 cc. of water. After half an hour the mixture was neutralized with sodium carbonate and poured into a cold solution of 25 g. of commercial cuprous cyanide in 25 g. of sodium cyanide and 150 cc. of water. The copious brown precipitate first formed evolved nitrogen when warmed to room temperature. The remaining oil was taken up with benzene, the benzene evaporated and the oil distilled, giving 15 g. of light yellow oil, b. p. 187–188° (corr.) at 14 mm. This gave a low nitrogen analysis.

Anal. Calcd. for $C_{13}H_9ON$: N, 7.17. Found: N, 6.65, 6.74.

Upon standing the oil partially solidified. The crystals were recrystallized from petroleum ether, giving colorless needles, m. p. 47°.

Anal. Calcd. for $C_{13}H_9ON$: N, 7.17. Found: N, 7.10.

Since the crude product gave a slight test for chlorine, the impurity present was probably *p*-chlorodiphenyl ether, as its boiling point would be close to that of the nitrile.

Upon hydrolysis with alcoholic potassium hydroxide the acid was formed in theoretical amount, m. p. 159–161°, which checks that previously obtained.[11]

o-Cyanodiphenyl Ether.—This was prepared similarly to the *p*-cyano derivative. The o-amine hydrochloride is readily soluble, which facilitates diazotization; yield, 15 g. of yellow oil, b. p. 188" (corr.) at 14 mm. Analysis for nitrogen gave low results.

Anal. Calcd. for $C_{13}H_9ON$: N, 7.17. Found: N, 6.75, 6.88.

The nitrile on hydrolysis gave the acid (m. p. 113°), which has previously received considerable attention because it offers a method for preparing xanthone.[12]

***p*-Bromo-*p*-nitrodiphenyl** Ether.—This has been previously prepared from *p*-bromophenol and *p*-nitrochlorobenzene.[2] Fifty grams of bromine was added slowly with stirring to a solution of 64.5 g. of p-nitrodiphenyl ether in 150 cc. of carbon tetrachloride. The mixture was then refluxed to complete the reaction. The solvent was evaporated and the residue recrystallized from 300 cc. of methyl alcohol; yield, 82 g. of white needles, m. p. 64"; reported previously, 65–66°.

***p*-Bromo-*p*-aminodiphenyl** Ether.—This was prepared by Le Fèvre and co-workers[7] but was not obtained in a pure state. The following method of preparation was found to be satisfactory: 29.4 g. of nitro compound was dissolved in 100 cc. of 95% alcohol,

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[8] Ullmann and Sponagel, *Ann.*, 350, 105 (1906).

[9] Haeussermann and Teichmann, *Ber.*, **29**, 1446 (1896).

[10] Ullmann, *ibid.*, **29**, 1881 (1896).

[11] Griess, *ibid.*, **21**, 980 (1888).

[12] Graebe, *ibid.*, **21**, 502 (1888).

18 g. of iron powder added and 10 cc. of concentrated hydrochloric acid run into the well-stirred mixture slowly, After four hours on the steam-bath, the mixture was filtered hot, the filtrate diluted with water and the precipitated amine recrystallized from methyl alcohol; yield, 22 g. or 84%; m. p. 109°.

Anal, Calcd. for $C_{12}H_{11}ONBr$: N, 5.28. Found: N, 5.32, 5.28.

p-Bromo-p'-acetaminodiphenyl Ether.—This was prepared in two ways: by bromination of the acetaminodiphenyl ether and by acetylating the amine. One cc. of bromine was added to 4.5 g. of the acetyl derivative dissolved in 30 cc. of acetic acid and the solution warmed for a minute. Upon cooling, the hydrabromide salt of the desired product crystallized out, 3.1 g. of slightly yeilow product, m. p. 180–183" (uncorr.), which lost its hydrogen bromide upon standing. Dilution of the filtrate gave 1.8 g. of the bromo-acetamino compound, which was also obtained by recrystallizing the hydrobromide salt from dilute alcohol, m. p. 162–163° (corr.).

Anal. Calcd. for $C_{14}H_{12}O_2NBr$: N, 4.57. Found: N, 4.59, 4.64.

Bromination of Diphenyl Ether.—To a solution of 85 g. (0.5 mole) of diphenyl ether in 100 cc. of carbon tetrachloride was added 80 g. (0.5 mole) of bromine slowly with occasional shaking. Hydrogen bromide was steadily evolved. When the reaction was complete. the solvent was distilled off and the residue fractionated under diminished pressure. There were obtained 20 g. of diphenyl ether, 59 g. of p-bromodiphenyl ether, b. p. 160–165° at 14 mm., and a residue of the dibromo derivative soluble in petroleum ether, together with a trace of higher brominated products insoluble in petroleum ether.

Summary

1. The nitration of diphenyl ether has been studied in detail and a satisfactory method for preparing the mononitro derivatives outlined.

2. Ortho and para aminodiphenyl ethers are easily separated by the difference in solubility of their sulfates.

3. A number of bromine derivatives of diphenyl ether have been prepared.

4. A bromine atom in one ring of diphenyl ether affects only slightly substitution in the second ring, which is in contrast to the influence of the nitro group.

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[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY, AND THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

SCHIFF BASES DERIVED FROM 5-CHLOROVANILLIN

BY RAYMOND M. HANN, GEORGE S. JAMIESON AND E. EMMET REID

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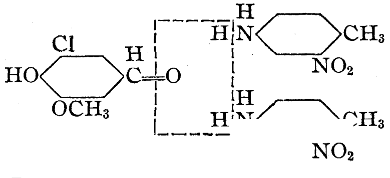
The intermolecular condensation of aldehydes and amines with subsequent loss of water leads to the formation of the well-known Schiff's bases. Compounds of this class containing the vanillin nucleus as an integral part of their structure have been investigated by a number of workers. Senier and Forster,[1] in carrying out a series of studies upon the thermotropic properties and the effect of actinic light upon Schiff's bases, prepared a series of vanillin amines. Hann[2] studied the effect of the introduction of iodine into the vanillin residue upon the thermotropic properties of the resulting bases when the iodinated aldehyde was condensed with various amines. Hann and Spencer[3] isolated chlorovanillalaniline and chlorovanillal-or-naphthylamine. 2-Bromovanillin and 6-bromovanillin have been condensed with benzidine by Raiford and Stoesser,[4] and a number of bases from 5-bromovanillin and 5,6-dibromovanillin have been prepared by Raiford and Hilman.[5]

In the present paper is described a further series of compounds of 5-chlorovanillin with aromatic amines. In a majority of cases the reaction products were obtained quite readily in crystalline condition upon cooling an organic solvent containing molecular proportions of the necessary components.

In one instance, that of m-toluidine, no crystalline product could be isolated although the marked deepening of the color as the reaction mixture was heated indicated a progressive formation of the chromophore C=N—. That this conclusion was warranted was proved by separation of the picrate of 5-chlorovanillal-*m*-toluidine upon addition of alcoholic picric acid. Hantzsch and Schwab[6] reported derivatives of a type in which one molecule of aldehyde condensed with two molecules of an amine, and in this study such a reaction product was encountered with nitro-p-toluidine. The reaction in this case may be considered to proceed in the following manner



Senier and Forster, J. *Chem. Soc., 107, 452* (1915).

Hann, J. *Wash. Acad. Sciences,* 14, 79 (1924).

Hann and Spencer, THIS JOURNAL, 49, 535 (1927).

Raiford and Stoesser, *ibid.,* 49, 1077 (1927).

[5] Raiford and Hilman, *ibid.,* 49, 1571 (1927).

[6] Hantzsch and Schwab, Ber., 34, 834 (1901).

Unsuccessful attempts were made to prepare derivatives of chlorovanillin with o- and *p*-nitro-anilines, 2,4-dichloro-aniline and trinitroaniline.

Experimental

The general procedure adapted was to weigh out 3 g. of chlorovanillin and an equimolecular proportion of the desired amine, add 25 cc. of 95% alcohol (or more if necessary for complete solution), heat to boiling and allow to digest at boiling temperature for two to two and one-half hours. Upon cooling, the reaction product usually separated in crystalline condition, or if an oil it could be induced to crystallize by scratching with a glass rod. The crude reaction product was recrystallized from alcohol to constant melting point, dried and analyzed. All melting points were taken with Anschiitz thermometers and stems totally immersed in the heating bath. Table I gives a summary of the results.

TABLE I

SCHIFF'S BASES DERIVED FROM 5-CHLOROVANILLIN

Name	Formula	Appearance	M. p., (corr.), °C.	Analysis (Kjeldahl–Gunning–Arnold Method) Wt., g.	0.1 N HCl consumed, cc.	Nitrogen, % Found	Calcd.
5-Chlorovanillal o-toluidine	$C_{15}H_{14}O_2NCl$	Almost colorless cryst. powder	115	0.1022	3.5	4.80	5.10
5-Chlorovanillal *p*-toluidine	$C_{15}H_{14}O_2NCl$	Canary-yellow glistening leaflets	142	1125	4.0	4 98	5.10
5-Chlorovanillal m-nitro-aniline	$C_{14}H_{11}O_4N_2Cl$	Light yellow powder	160	.1141	7.4	9 08	9 14
5-Chlorovanillal *p*-chloro-aniline	$C_{14}H_{11}O_2NCl_2$	Orange-yellow cryst. powder; light yellow with gentle heat	128	1548	4.8	4.34	4.73
5-Chlorovanillal cymidine	$C_{18}H_{20}O_2NCl$	Sl. yellow glistening truncated prisms	146–147	.1068	3 4	4.46	4.41
5-Chlorovanillal *p*-anisidine	$C_{15}H_{14}O_3NCl$	Brilliant straw-colored needle-like crystals	131	.2352	7.9	4.70	4.80
5-Chlorovanillal benzidine	$C_{28}H_{22}O_4N_2Cl_2$	Yellow powder	251–252	.1041	4.1	5 52	5.38
5-Chlorovanillal *m*-aminobenzoic acid	$C_{15}H_{12}O_4NCl$	Yellow hard cryst. crust	207	.1541	5 2	4.73	4.58
5-Chlorovanillal *p*-aminophenol	$C_{14}H_{12}O_3NCl$	Iridescent brick-red granules	150	.1229	4 3	4.90	5 05
5-Chlorovanillal *o*-dianisidine	$C_{22}H_{21}O_4N_2Cl$	Orange powder	188	,1226	5 8	6.63	6 79

The picrates of the Schiff's bases crystallize readily from alcoholic solutions and it is sometimes possible to obtain the picric acid addition product when the base itself cannot be isolated. In the present study the picrates were obtained by dissolving one gram of the pure base in 10 cc. of 10% alcoholic picric acid, heating to boiling and then allowing to cool, when the picrate separated. It was usually pure, but was recrystallized once from 95% alcohol before analysis. The results are given in Table II.

TABLE II

PICRATES OF SCHIFF'S BASES DERIVED FROM 5-CHLOROVANILLIN

				Analysis Salicyl sulfonic acid method			
Picrate of	Formula	Appearance	M. p. (corr.), °C.	Wt., g.	0.1 *N* HCl consumed, cc.	Nitrogen, % Found	Calcd.
5-Chlorovanillal m-toluidine	$C_{21}H_{17}O_9N_4Cl$	Soft granular yellow micro-crystals	224	0.1237	9.8	11.10	11.10
5-Chlorovanillal *p*-toluidine	$C_{21}H_{17}O_9N_4Cl$	Soft brilliant golden yellow needles	230	.1206	9.3	10.80	11.10
5-Chlorovanillal m-nitro-aniline	$C_{20}H_{14}O_{11}N_5Cl$	Orange iridescent cryst. crusts	190	.1062	9.6	12.66	13.08
5-Chlorovanillal p-chloro-aniline	$C_{20}H_{14}O_9N_4Cl$	Orange-yellow granules	215	.1298	10.0	10.79	10.67
5-Chlorovanillal p-anisidine	$C_{21}H_{17}O_{10}N_4Cl$	Bright orange needles	229–230	.1188	9.1	10.73	10.76
5-Chlorovanillal benzidine	$C_{40}H_{28}O_{18}N_8Cl_2$	Micro-cryst. fine orange powder	250–260 (dec)	.1660	13.3	11.22	11.44
5-Chlorovanillal[a] m-aminobenzoic acid alcoholate	$C_{21}H_{15}O_{11}N_4Cl \cdot C_2H_5OH$	Orange-red hard granules	241	.1079 .2036 g. lost	7.4 .0170 g. at 120°	9.61 8.35	9.65 7.93
5-Chlorovanillal p-aminophenol	$C_{20}H_{15}O_{10}N_4Cl$	Orange needles	224–225 (dec.)	.1712	13.2	10.80	11.06
o-Dianisidine	$C_{26}H_{22}O_{16}N_8$	Soft golden yellow needles	Darkens, dec. 225°	.1018	11.4	15.69	15.96
5-Chlorovanillal m-aminohenzoic acid	$C_{21}H_{15}O_{11}N_4Cl$	Orange-yellow powder	236	.1144	8.5	10.41	10.48

[a] Dried at 120° for five hours.

5-Chlorovanillal-*bis*-nitro-*p*-toluidine.—Five g. of nitrotoluidine (1-CH_3-2-NO_2-4-NH_2) and 6.1 g. of pure chlorovanillin were dissolved in 25 cc. of absolute alcohol and the solution was refluxed for two and one-half hours. Upon standing overnight in the ice box, the reaction mixture solidified to a mass of orange-yellow crystals. These were recrystallized twice from 95% alcohol, from which the compound separated in hard yellow flower-like crystalline rosets which melted at 125° (corr.) to a clear yellow oil. Although the experiment was repeated three times no compound formed by a condensation of a single amine molecule could be isolated.

The picrate of the *bis*-compound separated in bright yellow micro-crystals when one gram of base was treated with 10 cc. of 10% alcoholic picric acid. It melted, although not sharply, at 148° to a clear red oil.

Anal. Base, subs., 0.1697: 0.1 N HCl, 14.1 cc. Calcd. for $C_{22}H_{21}O_6N_4Cl$, 11.85. Found: 11.64. Picrate, subs., 0.2019: 0.1 *N* HCl, 20.1 cc. Calcd. for $C_{28}H_{24}O_{13}N_7Cl$: N, 13.97. Found: N, 13.94.

Summary

Chlorovanillin has been condensed with o-, m- and p toluidines, *m*-nitro-aniline, p-chloro-aniline, cymidine, *p*-anisidine, nitro-p-toluidine, benzidine, m-aminobenzoic acid, p-aminophenol and dianisidine, and the condensation products have been characterized by the preparation of their addition products with picric acid.

BALTIMORE, MARYLAND, AND WASHINGTON, D. C.

NOTES

Reduction with Alcohols of Cinnamaldehyde to Beta-Phenylpropionaldehyde.—It was shown in a previous paper[1] that acrolein was reduced over alumina by propanol at 330° according to the equation

$$CH_2{=}CHCHO + CH_3CH_2CH_2OH = CH_3CH_2CHO + CH_3CH_2CHO \qquad (1)$$

Since it seemed possible that this was a general reaction for 2,3-unsaturated aldehydes, and since it offered a means of reducing the carbon to carbon double bond without reducing the carbon to oxygen bond, attempts were made to reduce cinnamaldehyde to β-phenylpropionaldehyde according to the equation

$$C_6H_5CH{=}CHCHO + C_3H_7OH = C_6H_5CH_2CH_2CHO + C_2H_5CHO \qquad (2)$$

The reduction was performed by passing 100 g. of cinnamaldehyde dissolved in 100 cc. of propanol over 5 g. of alumina catalyst (from hydrated alumina) at 330° and at the rate of 75 cc. per hour. The liquid product was distilled at atmospheric pressure to remove the low-boiling fraction (propionaldehyde, propyl ether, propyl alcohol and water) and under a pressure of 40 mm. of mercury to separate the β-phenylpropionaldehyde. Twenty grams of β-phenylpropionaldehyde was obtained, b. p. 130–133" at 40 mm.; 55 g. of cinnamaldehyde was recovered, b. p. 155–158° at 40 mm.; and 15 g. of a dark brown, viscous liquid boiling above 250° remained. The β-phenylpropionaldehyde was identified by the preparation of the oxime which was recrystallized until it had a melting point of 97° (corr.). The melting point is given in the literature as 93–94.5°.

From the amounts of the products obtained, it is estimated that 35% of the cinnamaldehyde and 50% of the propyl alcohol introduced had reacted in some way. About 60% of the cinnamaldehyde which reacted was converted into β-phenylpropionaldehyde, the rest having undergone polymerization, decomposition, etc. About 50% of the alcohol which reacted was used in the formation of propionaldehyde and β-phenylpropionaldehyde, almost all of the remainder forming propyl ether, except a very small amount which was converted into propylene and water.

Similar reactions occurred and approximately the same yields of β-phenylpropionaldehyde were obtained using 50 g. of cinnamaldehyde in 100 cc. of methanol, ethanol or propanol.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

PAUL E. WESTON
HOMER ADKINS

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Acetoxymercuric Chloride, $CH_3COOHgCl$.—The replacement of hydrogen in organic compounds by mercury, mercuration, is practically always

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[1] Weston and Adkins, THIS JOURNAL, 50, 1930 (1928).

effected by the use of mercuric acetate.[1] Other mercuric salts, like the nitrate and sulfate, may be used less conveniently. Salts like mercuric chloride which are not hydrolyzed do not give the mercuration reaction. For instance, pure phenol can be refluxed for days with mercuric chloride without giving any organic mercury compound.[2] With mercuric acetate, phenol gives a mixture of mono- and di-mercurated products instantly.

Since the chloromercuri compounds are often easier to purify than the acetoxymercuri compounds, a common practice is to mercurate a substance with mercuric acetate and immediately add sodium chloride to produce the chloromercuri compound.

A double salt of mercuric chloride and mercuric acetate, $HgCl_2 \cdot Hg(OCOCH_3)_2$ is recorded in the literature.[3] It was thought that this might really be a mixed salt, $ClHgOCOCH_3$, and might be used as a mercurating agent to give the chloromercuri compounds directly. The results showed that the salt is actually a *mixed* instead of a double salt but that it cannot be used for mercuration.

The salt was prepared from equimolar quantities of mercuric chloride and mercuric acetate in water solution. Evaporation under a variety of conditions gave large clear rhombic crystals entirely different from either of the original substances.

Anal. Subs. 0.1745, 0.1729: Hg, 0.1185, 0.1173. Calcd. for $C_2H_3O_2ClHg$: Hg, 67.97. Found: Hg, 67.91, 67.84.

Dimethylaniline, phenol and *p*-cresol were selected as substances easy to mercurate.[1] From dimethylaniline a white crystalline product was obtained which gave no precipitate with sodium hydroxide but gave mercuric sulfide with hydrogen sulfide. It did not melt. It was therefore not a mercurated dimethylaniline but a molecular compound similar to that obtained from dimethylaniline and mercuric chloride. When the mixed salt was heated for two weeks with a large excess of pcresol in aqueous alcohol, inorganic mercury still remained. No mercurated cresol could be isolated. A similar negative result was obtained with phenol.

These results show not only that the acetoxymercuric chloride cannot be used in place of mercuric acetate as a mercurating agent but that it is very stable in solution. If it gave any appreciable amount of mercuric acetate in solution, the latter would mercurate the substances tested.

This mercuric salt should be subjected to a physical chemical study.

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FRANK C. WHITMORE
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[1] Pesci, *Z. anorg. Chem.*, **15**, 217 (1897); Dimroth, *Ber.*, **35**, 2044 (1902).

[2] Private communication from Louis Ehrenfeld.

[3] Donk, *Rec. trav. chim.*, **26**, 216 (1907).

Synthesis of *Iso*-amylcyclopentane.—*Iso*-amylcyclopentane was prepared by methods similar to those used by Chavanne and Becker in the synthesis of ethylcyclopentane.[1] *Iso*-amylcyclopentanol was prepared from cyclopentanone and *iso*-amyl bromide by a Grignard reaction; this alcohol was dehydrated with *p*-toluenesulfonic acid and the resulting cyclopentene was hydrogenated with platinum black as a catalyst.

The following physical constants were determined: *iso*-amylcyclopentanol—colorless, oily liquid, pleasant odor, b. p. 101° at 17 mm., d_4^{26} = 0.8848, n_D^{26} = 1.4549; *iso*-amylcyclopentene—colorless, mobile liquid, petroleum-like odor, b. p. 168–170° at 760 mm., d_4^{25} = 0.8010, n_D^{25} = 1.4467; iso-amylcyclopentane--colorless, mobile liquid, petroleum-like odor, b. p. 168–170" at 760 mm., d_4^{25} = 0.7837, n_D^{25} = 1.4321.

CONTRIBUTION FROM THE
INSTITUTE OF CHEMISTRY OF THE
UNIVERSITY OF LYONS
LYONS, FRANCE

JOHN MCARTHUR HARRIS, JR.

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NEW BOOKS

Volumetric Analysis. By I. M. KOLTHOPP, Professor of Analytical Chemistry at the University of Minnesota, with the collaboration of Dr. Ing. H. MENZEL, Dresden. Translated by N. HOWELL FURMAN, Ph.D., Associate Professor of Analytical Chemistry, Princeton University. Vol. II. Practical Volumetric Analysis. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1929. xiv + 552 pp. 18 figs. 15 X 23.5 cm. Price $5.00.

This book represents, beyond all question, a scholarly, interesting and valuable contribution to the literature of analytical chemistry and one which deserved translation. The original intention had been to write merely a treatise on the underlying theories of titration methods with the idea that H. Beckurt's revision of F. Mohr's well-known book would still serve as a text-book of practical methods, but since the publication of the Beckurt book there has been such a marked development in this branch of analytical chemistry that it seemed wise to write a new, critical and comprehensive work. The text of Beckurt, however, has been used freely in the preparation of this new book. To give some idea of the thoroughness with which Dr. Kolthoff has combed the journal literature, it may be mentioned that there are about one thousand footnotes and in one case more than fifty references are given in a single footnote. There is hardly a paper written during the last fifteen years on volumetric procedure that does not receive consideration or mention.

The book is not intended as a text for beginners. The discussion presupposes a considerable knowledge of chemical principles and only rarely are the directions given in sufficient detail for the beginner to follow.

[1] Chavanne and Becker, Bull. *soc. chim. Belg.*, 36, 591 (1927).

Moreover, for the sake of completeness many methods are mentioned which have not been found useful and the beginner could not fail to become bewildered by the mass of material contained in such a small space.

The book, despite its title, is not written for the practical man who merely wants to know how to make analyses and get results. Such a person cares little for the scientific explanation of the chemical principles involved and is more interested in the analysis of ores than of solutions of fairly pure substances. He wants to know the best method, if such there be, rather than all possible methods that are good. In this book, for example, the ferrocyanide method of titrating zinc solutions is considered in considerable detail, and the results of some careful experimentation by the author are given (although he overlooked the excellent monograph by Nissenson and credited to W. W. Scott a method recommended by F. G. Breyer of the New Jersey Zinc Co. in Scott's book). For the analysis of zinc ores, on the other hand, the reader is referred to the voluminous work of Lunge–Berl and this is the very thing that will interest the practical man.

The comments which Dr. Kolthoff makes upon the various methods are interesting and good. For the most part, chemists will agree with his conclusions. Outside of the book by Clark and Lubs, there is probably no English text that compares with this in the discussion of suitable indicators for neutralization titrations. Again, with respect to the selection of proper standards, the discussion is most painstaking and methods of testing and preparing many suitable standards are given.

Besides the usual methods of acidimetry and alkalimetry, oxidation–reduction and precipitation, methods are given involving the use of potassium bromate, potassium iodate, ceric sulfate and titanous chloride as titrating agents. The methods include the examination of organic substances and all sorts of nitrogen compounds, as well as inorganic substances.

The work of the translator has been faithfully done and he has included, with the cooperation of Dr. Kolthoff, about fifty pages of material not found in the original text. The book is practically free from misprints. At times the translation is too literal and the English rather awkward. Thus the use of the word performance on page 205 instead of *procedure* is a little unusual and the sentence on page 46, "The test of utility by means of *very* exactly performed titrations, on *the* other hand, remains after it has been once *performed*," is just a bit difficult to understand and arises from the attempt to translate literally. So faithful to the original text has Dr. Furman been, that he gives an atomic weight table as published in 1925 rather than change a figure in the original text.

Acting upon the suggestion of Schoorl, Kolthoff enthusiastically advocates the use of "rational" rather than "international" atomic weights because the more accurate values are based upon weighings corrected for air displacement. Thus he gives three atomic weight tables in the book, one of international atomic weights for 1925, Schoorl's *rational* table and one of atomic weights rounded to 0.1 per cent. In the opinion of the reviewer this practice is more likely to lead to confusion than if the latest table of international atomic weights is used alone. Schoorl's point may be a good one but there is little chance of the *rational* table being adopted. It is most important that chemists should all use the same atomic weights to avoid confusion.

W. T. HALL

Analytical Chemistry. Volume II. Quantitative Analysis. Based on the text of F. P. TREADWELL, Late Professor of Analytical Chemistry at the Polytechnic Institute of Zurich. Translated, enlarged and revised by WILLIAM T. HALL, Associate Professor of Analytical Chemistry, Massachusetts Institute of Technology. Seventh edition. John Wiley and Sons, Inc., New York, 1928. xiii + 848 pp. 152 figs. 15 X 23.5 cm. Price, $6.00.

The seventh edition contains numerous minor changes and a syllabus of the two semester course in analytical chemistry as given to students of chemical engineering at the Massachusetts Institute of Technology.

Considering the size and contents of the book, the material has been brought up to date in the case of magnesium and others but in the case of potassium the improvements of Smith and others have been omitted. It may be necessary in another edition to omit the details of methods which are obsolete and unreliable since they are only of historical importance. It is highly desirable that the relative precision and accuracy of the various methods of analysis of the same constituent be given.

A considerable amount of the theory is taken up in the class room, according to the syllabus. This feature necessitates references to other textbooks and articles in the journals. In this connection some space should be devoted to constant-boiling hydrochloric acid.

The milliequivalent of iodine is given as 0.12685 (p. 553) instead of 0.12693. The word "currents" (p. 464) was erroneously used in the electrometric titration discussion.

The book is surprisingly free from typographical errors.

The foregoing statements are suggestions from the ideal standpoint. Treadwell and Hall's book is and should be in the library of every chemist who aims to do precise and accurate analysis.

STEPHEN POPOFF

Photometric Chemical Analysis (Colorimetry **and** Nephelometry). Vol. II. **Nephelometry.** BY JOHN H. YOE, Ph.D., Professor of Chemistry, University of Virginia. With contributions by HANS KLEINMANN, M.D., Ph.D., University of Berlin. John Wiley and Sons, Inc., New York, 1929. xvi + **337** pp. **44 figs.** 15 X 23.5 cm. Price, $4.50.

Nephelometry and the rapid development that this branch of chemical analysis has undergone within the past decade are well epitomized in

Volume II of "Photometric Chemical Analysis." The latter initiates a systematic discussion of a subject which has heretofore been accessible only in scattered publications. Part I of "Nephelometry" is devoted to the history and description of various types of nephelometers, directions for use, nephelometric research and the theory of nephelometry. The remaining two parts discuss various inorganic and organic determinations, respectively. In the inorganic section comprising Part II the determinations of ammonia, arsenic, calcium, chlorine, phosphorus and sulfur are described in detail, while nephelometric procedures for acetone, amylase, dichloro-ethyl sulfide, fats, lipase, nucleic acids, pepsin, proteins, purine bases and trypsin constitute Part III. From a critical point of view it would appear that the chapter on the theory of nephelometry could be amplified to the distinct advantage of the book and might well include a discussion of coalescence and the factors influencing particle size. On the other hand, the discussion of the nephelometric constant appears to be somewhat labored. Furthermore, it will probably prove advantageous in future editions to transfer some of the material, such as the bisulfite method for lead and the ferrocyanide method for zinc, of Volume I to Volume II. These are nephelometric rather than colorimetric methods.

The thanks of all who are interested in this type of analytical procedure are due the author for so adequately crystallizing the literature of nephelometry and presenting it within such convenient compass.

LAWRENCE T. FAIRHALL

The Industrial Development of Searles Lake Brines. By JOHN E. TEEPLE, Ph.D., Consulting Chemist and Chemical Engineer. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York City, 1929. 182 pp. 60 figs. 15.5 X 23.5 cm. Price, $3.00.

It is a great pleasure to American chemists, whether in the industrial or the theoretical field, to have at last this story of the Searles Lake development, which all have heard about and but few have known about. Now at last we can know something about it—not all, by a large margin, but still a great deal; and all American chemists can now have a substantial pride both in the success of an immensely important enterprise, and in the courage which Dr. Teeple has shown in publishing some of the real facts about the work. Perhaps Dr. Teeple doesn't think that it has required courage to give the world the data on this magnificent piece of phase-rule work; but whatever it is that has given us the result, Dr. Teeple has it to an extent that is commendable, and it is to be hoped that his example may be copied.

Part I of the book gives a running tale of the history and development of the plant. The Searles Lake brine is essentially a seven-component system. The commercial output consists of pure potassium chloride and borax. The separation has required a carefully designed and well operated plant—which means good chemical engineering; and it has required an exact knowledge of the various equilibria possible in this system at a variety of temperatures—which means good physical chemistry. The combination is not new, but it has not been overworked in this country. May this book convince many that it is a profitable combination!

Part II contains the equilibrium data and diagrams. Under the *32* headings there are given data for sixteen systems of two components, thirty-eight of three components, and one of six components; some are reported on at one temperature only, many of them at several temperatures. The sulfates, carbonates, borates and chlorides of sodium and potassium form the majority of the systems. For each isotherm, the composition of the isothermally invariant solutions is given in units of weight and in molar units; the univariant systems are usually represented by straight lines. The sum total of this huge mass of data can be appreciated only after careful study. It is a compilation of phase-rule work which has no equal in American chemistry, and ranks with the classic investigations of van't Hoff and his colleagues on the Stassfurt salt deposits. There is very clearly still more to be printed about these systems, and it is to be hoped that in time each of them will be given to us in the detail necessary for complete usefulness. May Dr. Teeple and his coworkers thus increase still further our debt to them for this admirable investigation.

ARTHUR E. HILL

Anorganische und Organische Entfärbungsmittel. (Inorganic and Organic Decolorizing Agents.) By Dr. LEOPOLD SINGER, Vienna. Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1929. xi + 251 pp. 15.5 X 22.5 cm. Price, unbound, R. M. 20; bound, R. M. 21.50.

The author points out that in spite of the increasing importance of decolorizing agents no comprehensive summary of the work that has been done upon them exists. The present volume is designed to fill this gap. The field is, however, so large that the author has restricted himself to a consideration of the articles and patents that have appeared since the war.

Both inorganic and organic decolorizing agents, that is, both decolorizing earths and decolorizing charcoals are covered. The headings of the chief chapters are as follows: Occurrence, Properties, Theories of Decolorization, Manufacture, Use, Regeneration. At the end of the book, there is an excellent list of the patents dealing with decolorizing agents.

The treatment is intentionally non-critical; it is also brief in its discussion of the separate articles and there is no claim for completeness. The book is valuable in that it furnishes a convenient and reasonably complete compendium of the recent work on decolorizing agents. It will surely be of great use to investigators in this field.

ARTHUR B. LAMB

The Pyrolysis of Carbon Compounds. BY CHARLES DEWITT HURD, Associate Professor of Chemistry, Northwestern University. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Ave., New York, 1929. 807 pp. 15.5 X 23.5 cm. Price, $12.50.

The pyrolysis of carbon compounds is a branch of organic chemistry that is rapidly growing in importance from both the practical and theoretical point of view. Processes involving pyrolysis are being used in industry extensively and, to a limited degree, in the interpretation of the mechanism of the severing of molecules by heat. Much of the work in this field of organic chemistry has been largely empirical. There is a great opportunity at present to extend the work through experimentation planned to gain clearer concepts in regard to the strength of the forces of attraction between atoms and to the variations in electron affinities associated with changes in structure. The appearance of this monograph is, accordingly, especially timely.

The author has been particularly successful in gathering the large amount of material scattered throughout the literature. Much of it, no doubt, could not be found by consulting indexes only. The extensive array of facts has been well systematized and is presented in an interesting way. Wherever the facts warranted generalizations, they have been made. The several chapters deal with the various types of compounds, such as hydrocarbons, halogen compounds, acids, esters, etc. Molecular rearrangements produced by heat are considered in addition to reactions of decomposition.

On account of the large number of facts assembled, the author felt it inadvisable to include any consideration of the effects of catalyzers in reactions of pyrolysis. One naturally is averse to prolonging a book beyond 800 pages. It is the opinion of the reviewer, however, that even a brief treatment of the effect of catalyzers on the pyrolysis of the several classes of compounds would have added to the excellence of the book.

This monograph should be available to all students specializing in the study of organic chemistry, and to research workers in industrial laboratories. The author has accomplished a real service, which will lead to increased activity in the study of an important division of the science.

JAMES F. NORRIS

The Journal of the American Chemical Society

VOL. 51 SEPTEMBER, 1929 No. 9

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

ACTIVITY COEFFICIENTS OF CADMIUM CHLORIDE AND BROMIDE

BY WALTER W. LUCASSE

RECEIVED NOVEMBER 6, 1928 PUBLISHED SEPTEMBER 5, 1929

When this investigation was started, the only recent electromotive force data from which the activity coefficients of the cadmium halides could be calculated were those of Horsch for cadmium chloride. His measurements using cadmium amalgam, led to values of the electromotive force for cells of the type

$$Cd \mid CdCl_2 \mid AgCl \mid Ag$$

and covered the range from very high dilution up to 0.0074 M with single points at 0.0995 and 6.62 M. In view of the peculiar properties of the cadmium halides, the low conductance ratios of their aqueous solutions, their tendency to form complex ions and other anomalous behaviors, it seemed well to study cells of this type somewhat more fully at higher concentrations and to extend the work to the other halides.

In the present paper are given results of measurements of cells of the type

$$Hg, Cd \mid CdCl_2 \mid AgCl \mid Ag$$

and

$$Hg, Cd \mid CdBr_2 \mid AgBr \mid Ag$$

from 0.01 M to 6 M and from 0.01 M to 3 M, respectively.

Recently Getman[2] has published values for the activity coefficients of the cadmium halides calculated, however, from measurements of cells using as the negative electrode mercury and the appropriate mercurous halide, except in the case of cadmium iodide where two series of determinations were made, one with silver–silver iodide electrodes and the other with lead amalgam–lead iodide electrodes.

Apparatus, Materials and Procedure.—The cell used was of the simplest type, being in the form of a straight tube about 2 cm. in diameter and 15 cm. in height. Connection

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[1] Horsch, THIS JOURNAL, 41, 1787 (1919).

[2] Getman, *J. Phys. Chem.*, **32**, 91 (1928); 32, 940 (1928).

with the amalgam in the bottom of the tube was made by means of a sealed-in platinum wire. The other electrode was supported in the upper part of the solution by means of a rubber stopper which served also to prevent evaporation.

The electrodes were made in the manner described by Noyes and Ellis,[3] the silver being formed from silver oxide as was done by Lewis.[4] The silver chloride or bromide was formed on the electrode by making it the anode in a 0.75 M hydrochloric or hydrobromic acid solution for about five hours with a current of 0.004 ampere. A number of different sets of electrodes were made up throughout the course of the investigation, replacement being necessary more frequently with the bromide than with the chloride electrodes. Before using, the electrodes were tested against each other in each case in order to make sure that no inconsistencies were introduced from this source.

The cadmium amalgam was made by electrolyzing a solution of cadmium sulfate over a mercury cathode. When the electrolysis was completed the amalgam was allowed to flow into a small evacuated flask which was then pumped out until the last traces of moisture had been removed. As soon as it had been sealed off the flask was inverted and set aside for several days so that any oxide might rise to the surface and thus be removed. Finally, the lower part of the amalgam was allowed to flow into a large evacuated flask containing such an amount of mercury as to bring its concentration to that used. Just before making a series of determinations a quantity of the amalgam was drawn into an evacuated tube so built that a stream of hydrogen could be passed over the amalgam as it was being transferred into the cell.

Standard solutions of cadmium chloride and bromide were prepared by dissolving the purified salts in conductivity water and the concentration was determined by gravimetric analysis. These standard solutions were then diluted quantitatively by weight with boiled, twice distilled water to give the solutions used in the measurements.

In making the electromotive force measurements, the solution was introduced into the empty cell and after placing the silver–silver halide electrode in position, the cell was suspended in the thermostat. It was allowed to remain thus for about four or five hours in order to come to temperature and so that the electrode might come to equilibrium with the solution. At the end of this time, the electrode was removed for an instant while a few cc. of the amalgam were introduced. A reading of the electromotive force was immediately taken, followed by others at about half-hour intervals for the next three hours. The first reading showed no definite trend of variation from the subsequent ones but frequently, due perhaps to the temperature change caused by introducing the amalgam, varied more widely from the later readings than they did among themselves. In such cases the first reading was disregarded. Otherwise a mean of all of the readings throughout this period was taken as the value of the cell. The variation of the accepted readings was always very slight, never more than five hundredths of a millivolt, and showed no particular trend. In several cases the cell was allowed to stand for twenty-four hours after taking these readings. It was usually found at the end of this time that the electromotive force had dropped slightly, never, however, more than half a millivolt. All measurements were made at 25 ± 0.01°.

Results

In Table IA are given the results obtained from the cells containing cadmium chloride. The first column gives the molality of the solution (moles of salt per 1000 g. of water) and the second the observed electromotive force. Plotting these values led to a smooth curve continuous

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[3] Noyes and Ellis, THIS JOURNAL, 39, 2532 (1917).

[4] Lewis, *ibid.*, 28, 166 (1906).

TABLE IA

THE ACTIVITY COEFFICIENTS OF CADMIUM CHLORIDE

m	E'	E	γ (Obs.)	γ (Calcd.)
(0.01)	(0 7409)	(0.5837)	0.503	0.503
.01010	.74058	.58338	.503	.502
.02015	.72212	.56492	.407	.413
,03030	.71183	.55463	.353	.358
.05056	.69953	.54233	.291	.293
.06968	.69227	.53507	.255	.255
.08145	.68881	.53161	.239	.236
.1000	.68431	.52711	.219	.214
.2014	.67003	.51283	.157	.147
.3027	.66241	.50521	.128	.118
.5101	.65338	.49618	.096	.090
.6908	.64849	.49129	.080	.078
.7962	,64629	.48909	.074	.075
.9999	.64235	.48515	.065	.071
2 045	.63165	.47445	.042	.085
4 227	.61899	.46179	.028	..
5.133	.61481	.45761	.026	..
6.146	.61050	.45330	.024	..

TABLE IB

$m \times 10^4$	1.527	2.144	3.363	3.659	4.79	9.24	25.81
γ (L. and R.)	0.930	0.933	0.905	0.901	0.872	0.809	0.697
γ	.954	.935	.901	.895	.882	.809	.696

with one obtained from the results of Horsch (E_2, Table II, of his paper) save for a displacement of 0.0686 volt. This displacement represented largely the difference in electromotive force of the cell with pure cadmium and with the amalgam of the concentration used but was due in part also to the differences in the potentials of the silver–silver chloride electrodes used. The electrodes used by Horsch were made by electrolytic deposition and when measured against hydrogen in 0.01 M hydrochloric acid led, upon taking 0.00924 as the value of the activity of H^+ and Cl^-, to the value −0.2258 for the standard silver–silver chloride potential. Electrodes made in the manner indicated above have been carefully studied and found to lead to a value of −0.2233. Taking into account this difference in the electromotive force[3,5] contributed by the silver–silver chloride electrodes in the two series, the correction to convert the electromotive force of the cell measured to what would be obtained with pure cadmium electrodes amounts to 0.0661 volt.

The activity coefficient of the electrolyte may be calculated from the electromotive force of a cell of the type used by means of the equation

$$E = E_0 - \frac{RT}{nF} \ln (4m^3\gamma^3) \qquad (1)$$

This equation upon introducing the numerical values, including that of

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[5] *See also Gerke, Chemical Reviews, 1,* 377(1925).

the standard electrode potential of cadmium as calculated by Lewis and Randall[1,6] (0.3976), becomes for calculating the activity coefficient

$$\log \gamma = 4.28026 - \log m - 11.27\,E \qquad (2)$$

To the values of the measured electromotive force as given in the second column, 0.0661 volt was added as indicated above and from the result there was subtracted the value of the standard potential of the silver–silver chloride electrode (0.2233). In this manner were obtained the values of E given in Col. 3, from which the values of the activity coefficients in Col. 4 were calculated by means of Equation 2.

In Table IB are given values of the activity coefficient at certain concentrations calculated from the data of Horsch. In the first row are given the concentrations (molality X 10^4) and in the second the values of the activity coefficients at the corresponding concentrations as calculated by Lewis and Randall[7] on the assumption that at very high dilutions the values are the same as for barium chloride. In the third row are given values calculated in the same manner as those in Part A using, however, the value for the silver–silver chloride potential found by Horsch. The points determined by Horsch at the four lowest concentrations have been omitted because of the experimental uncertainty in this region. Both calculations lead to identical results at the concentrations higher than those given in IB (*i. e.*, at 0.003519, 0.0074, 0.0995 and 6.62 M). Due to a difference in interpolation between 0.0074 and 6.62 *M*, the values given by Lewis and Randall at round concentrations between 0.01 and 0.1 M vary considerably, especially at the lower concentrations, from those here given.

Above 0.05 M the values given in Table IA agree satisfactorily with those of Getman. Below this point, however, there is a marked difference in the form of the two curves, the values determined by Getman rising much more rapidly with increasing dilution. In Table II are given the results from cells containing cadmium bromide. The column headings have the same significance as in Table IA and the method of calculation was the same. The value of the standard potential of the silver–silver bromide electrode[8] was taken as 0.0734 and after correcting in the same manner as above to the value of the electromotive force with pure cadmium as electrode the calculation was made from the values in Col. 3 by means of Equation 2.

Above 0.02 M the agreement between these values of the activity coefficient and those given by Getman is satisfactory. Below this concentration there is again a sharper rise in his values than would be indicated by the points given here.

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[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 419.

[7] Lewis and Randall, ref. 6, pp. 361–362.

[8] Lewis and Storch, THIS JOURNAL, **39**, 2544 (1917); see also Livingston, *ibid.*, 48, 45 (1926).

TABLE II

THE ACTIVITY COEFFICIENTS OF CADMIUM BROMIDE

m	E'	E	γ (Obs.)	γ (Calcd.)
0.01000	0.59319	0.58589	0.476	0.440
.01386	.58459	.57729	.429	.425
.01993	.57563	.56833	.376	.364
.02801	.56734	.56004	.332	.326
.03997	.55914	.55184	.288	.288
.05629	.55147	.54417	.249	.252
.08114	.54357	.53627	.212	.216
.1000	.53952	.53222	.191	.196
.1378	.53337	.52607	.163	.168
.2026	.52640	.51910	.133	.137
.2724	.52140	.51410	.113	.116
.4069	.51486	.50756	.089	.091
.5444	.51011	.50281	.075	.076
.8056	.50404	.49674	.060	.060
.9996	.50054	.49324	.053	.053
1.314	.49577	.48847	.045	.045
1.896	.48878	.48148	.038	.037
3.0815	.47773	.47043	.031	.034

Discussion

The above method of computing the activity coefficient, because of using their value of the standard electrode potential of cadmium, is essentially accepting the extrapolation of Lewis and Randall[9] as a basis and was resorted to after attempts had failed to fit the data satisfactorily to the functions of Hückel and Brönsted.[10] This was due, very probably, to the presence of complex ions[11] whose equilibria would have to be taken into account in order to work out such a solution. It is possible also that the introduction of the higher terms[12] of the Debye-Hückel theory might lead to a more satisfactory expression of the results.

However, the deviations from the limiting law, unless very large errors have been made in the above assumptions, take place in an unusual manner and become apparent at very low concentrations. This can be seen from Table III, in which are given the values of the activity coefficient at very high dilutions. In the first column is given the molality and in the second the corresponding value of the activity coefficient of a bi-univalent electrolyte as calculated by the equation

$$\log \gamma = -1.749 \sqrt{m}$$

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[9] The calculation of the activity coefficients of cadmium chloride would have been considerably simplified by accepting their value at some one concentration but, considering also the cadmium bromide, the method used seemed preferable.

[10] Hückel, *Physik. Z.*, **26**, 93 (1925); Brönsted, THIS JOURNAL, 44, 938 (1922).

[11] McBain and Van Rysselberge, *ibid.*, 50, 3009 (1928).

[12] Gronwall, La Mer and Sandved, *Physik. Z.*, 29, 358 (1928). So far this has been applied only to symmetrical types.

TABLE III

THE: ACTIVITY COEFFICIENTS OF BI-UNIVALENT ELECTROLYTES AT HIGH DILUTIONS

$m \times 10^4$	γ, lim. func.	γ, $BaCl_2$	% diff.	γ, $CdCl_2$	% diff.
1.029	0.960	0.961	0.1	1.000	4.1
1.087	.959	.960	.1	1.042	8.7
1.137	.958	.959	.1	1.028	7.3
1.269	.956	.957	.1	1.004	5.0
1.527	.951	.953	.2	0 954	0.3
2.144	.943	.945	.2	.935	−0.8
3.363	.929	.932	.3	.901	−3.0
3.659	.926	.929	.3	.895	−3.3
4.79	.916	.920	.4	.882	−3.7
9.24	.885	.893	.9	.809	−8.6
25.81	.815	.834	2.3	.696	−14 6
35.19	.788	.812	3.0	.652	−17.3
74.0	.707	.751	6.2	.568	−19.7

a form to which the limiting function of Debye and Huckel may be reduced.[13] In the third column are given the values of the activity coefficient of barium chloride as calculated from the equation of Huckel using the constants obtained by Harned.[14] The equation agrees very well with the experimental data and we have assumed that it holds likewise at low concentrations. The percentage difference between the two values is given in the following column and indicates the magnitude of the deviation from the limiting law which might be expected in the case of a bi-univalent electrolyte. The fifth column gives the values of the activity coefficient of cadmium chloride as calculated above from the data of Horsch. The relatively large deviations given in the last column between these values and those calculated by the limiting law indicate the marked difference in the behavior of cadmium chloride from that of the more typical bi-univalent electrolytes.

The relation between the values of the activity coefficients of cadmium chloride and bromide given above and the molality can be expressed with a fair degree of accuracy over a considerable concentration range by the equation of Harned[15]

$$\log \gamma = \alpha m - \beta m^{\alpha'}$$

The constants a, β and a' were found to have the values 0.6, 1.75 and 0.38 for cadmium chloride and 0.2, 1.48 and 0.308 for the bromide. The activity coefficients calculated by these equations are given in the last columns of Tables I and II. By changing the constants somewhat closer agreement with the experimental values over shorter or over different

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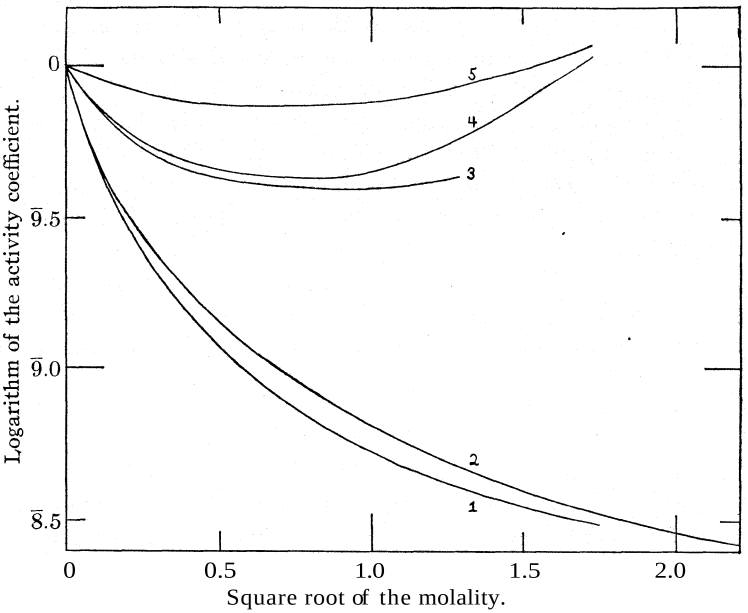
[13] Debye and Hückel, *Physik. Z.*, 24, 185 (1923); see also Brönsted and La Mer, THIS JOURNAL, 46,555 (1924).

[14] Harned, *ibid.*, 48,326 (1926).

[15] Harned, *ibid.*, 42, 1808 (1920); 44, 252 (1922); Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Company, New York, 1924, p. 744.

concentration ranges could be obtained. This would be without point, however, in view of the uncertainty of the extrapolation.

How different the behavior of the cadmium halides is from that of typical strong electrolytes can be seen further from Fig. 1, where the logarithms of the activity coefficients of cadmium chloride and bromide from Tables I and II, of lithium chloride from the data of MacInnes and Beattie[16] and of barium and strontium chloride are plotted against the square root of the molality. The curves of the alkaline earth chlorides all exhibit minima at concentrations below 0.7 M.[17] The activity coefficients of the cadmium halides show little if any such tendency even at very high concentrations. The point determined by Horsch at 6.62 M cadmium chloride leads to the value 0.025 for the activity coefficient and taken in conjunction with the values given in Table I might indicate a slight minimum in the region of the nearly saturated solution. However, from the general form of the three curves this seems unlikely. At moderate and high concentrations the values of the activity coefficients of the cadmium halides fall much below those of a typical bi-univalent electrolyte. Thus the values for cadmium chloride at 0.01, 0.1 and 1 M are 0.503, 0.219 and 0.065 as against



1, $CdBr_2$; 2, $CaCl_2$; 3, $BaCl_2$; 4, $SrCl_2$; 5, LiCl.

Pig. 1.—The activity coefficients of cadmium chloride and bromide and typical strong electrolytes.

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[16] MacInnes and Beattie, THIS JOURNAL, 42, 1117 (1923).

[17] Lucasse, *ibid.*, 47, 743 (1925).

0.723, 0.499 and 0.397 calculated by Harned for barium chloride at the same concentrations.

By the nature of their assumption the values of the activity coefficient of cadmium chloride calculated by Lewis and Randall lie everywhere below those of barium chloride except at very high dilutions, where they are considered to be equal. Thus the values given at the first four concentrations in Table IB are considered to be the same for both salts. It seems not unlikely, however, that at very high dilutions the values for cadmium chloride might rise slightly higher than those for barium chloride. However, in view of the uncertainty of the data in this region and the very slight differences in the values of the activity coefficients of the alkaline earth chlorides at 0.0001 M (all very nearly 0.961) as calculated by the equation of Hückel, using the constants determined by Harned, it cannot be regarded as significant that the values given in Table IB cross in the neighborhood of 0.0003 M, below which concentration the values for cadmium chloride are markedly higher (0.970 at 0.0001 M) than those for barium chloride.

If the cadmium halides behave like typical strong electrolytes at all, it is only at extremely low concentrations. At moderate and high concentrations their behavior becomes such as to preclude them unquestionably from consideration as completely dissociated.

Summary

In the above paper are given values of the electromotive force at 25° of the cell Hg, Cd | CdX_2 | AgX | Ag. The concentrations of the cadmium chloride and bromide, represented by CdX_2, were varied from 0.01 to 6 *M* and from 0.01 M to 3 M, respectively.

From these data values of the activity coefficients of the salts have been calculated over these concentration ranges.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE TRANSFERENCE NUMBERS OF CADMIUM CHLOFUDE AND BROMIDE

BY WALTER W. LUCASSE

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The transference numbers of an electrolyte can be calculated from the results of measurements of concentration cells with liquid junction if the activity coefficient of the electrolyte is known as a function of the concentration. In the present paper are given values of the electromotive force of cells of the type

$$\text{Ag} \mid \text{AgX} \mid \text{CdX}_2\ (0.1\ \text{M}) \mid \text{CdX}_2\ (m) \mid \text{AgX} \mid \text{Ag}$$

in which X represents the chloride or bromide ion, and m is varied from 0.01 to 6 M and from 0.01 to 3 M, respectively. The preceding paper gives values of the activity coefficient over these concentration ranges.

The solutions were the same as those used in measuring the cells without liquid junction and the electrodes were made up in the same manner. The cells used were the same as those in a previous study[1] and consisted of three parts, the middle compartment containing an approximately one-to-one mixture of the solutions surrounding the electrodes in the end compartments. In each case about four hours were allowed to elapse between the time the cell was introduced into the thermostat and the time of taking the first reading. From four to six readings were then taken at half-hour intervals, the mean of which was accepted as the value of the cell. The variation in these readings was always very slight, seldom more than a few hundredths of a millivolt. All measurements were made at 25 ± 0.01°.

In Col. 3 of Table I are given the values of the electromotive force of the above cell at the molality (moles of salt per 1000 g. of water) given in the first column. To facilitate comparison the corresponding normal concentrations (equivalents per liter of solution) are given in the second column.

The method used in calculating the transference numbers was the same as that for the alkaline earth chlorides[2] which, although a somewhat disadvantageous modification of the method of MacInnes and Beattie,[3] was

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[1] Lucasse, *J. Phys. Chem.*, 30, 562 (1926).

[2] Lucasse, THIS JOURNAL, **47**, 743 (1925). See, however, Jones and Dole, *ibid.*, **51**, 1073 (1929). In the present case a method depending upon algebraic analysis, although highly desirable, would be more difficult of application than in the case of barium chloride, in part because of the failure to find a suitable relationship between the concentration and the activity. The dangers inherent in the graphical method have been reduced to some extent by taking into account also the ratios of the electromotive force values of the two types of cells between each concentration interval. The form of the curve and the accuracy of the values, especially below 1 M, are as nearly true, it would seem, as can be obtained from the data at the present time.

[3] MacInnes and Beattie, *ibid.*, **42**, 1117 (1920).

TABLE I

THE TRANSFERENCE NUMBERS OF CADMIUM CHLORIDE

m	*N*	*El*	Log *A*	t_+
(0 01)	0 0199	+(0.02670)	0.90227	0.486
.01010	,0201	+ .02652	0.90655	.485
,02015	.0401	+ .01766	1.11461	.466
,03030	.0603	+ .01290	1.22994	.460
.05056	.101	+ ,00729	1.36847	.463
,06968	.139	+ .00382	1.45025	.472
,08145	.162	+ .00214	1.48996	.479
.1000	.199	.00000	1.54108	.487
.2014	.399	– .00697	1,70062	.498
.3027	.599	– .01067	1.78895	.494
,5101	1 00	– .01523	1.89059	.471
.6908	1.35	– .01747	1 94315	.445
.7962	1 55	– 01859	1,97095	.425
.9999	1.93	– .02033	2.01368	.386
2.045	3 82	– ,02459	2 13450	.241
4.227	7 32	– ,02736	2.27393	.002
5.133	8.62	– 02712	2 32613	– 104
6.146	10.0	– ,02653	2.36940	–.192

here employed for the same reasons as given in the earlier paper. For a bi-univalent electrolyte the transference number of the cation is related to the electromotive force of a cell of the above type and the activity by the equation

$$dE_t = -t_+ \frac{3RT}{2F} d \ln a_\pm$$

The values of E_t were therefore plotted on a large scale as ordinates against the values of log A, at the corresponding concentrations, given in Col. 4. These latter (log A = 1000 log *a,)* were obtained from the preceding paper. The slope of the curve (dE_t/d log A) at each value of log A was then determined graphically and divided by the constant factor $3RT/2F$ (*i. e., 0.088733).* Finally, the values of the transference number thus obtained were plotted against log A and the values given in the last column of the table read directly from the smooth curve passing through the points.

In Table II are given the results obtained from the cells containing cadmium bromide. The column headings have the same significance as in the previous table.

Data at 25° with which to compare these results are very meager. However, Jahn and his associates have made a number of measurements of the transference numbers of cadmium chloride, bromide and iodide at 18° in solutions from about *0.005* to about *1* N by gravimetric methods.[4] His highest concentration for the bromide is about *1.1* N and up to this point the agreement is very satisfactory. Beyond this point the values continue to decrease, passing through zero at about 2.7 N to negative

[4] Jahn, *Z. physik. Chem.,* 37,673 (1901).

TABLE II

THE TRANSFERENCE NUMBERS OF CADMIUM BROMIDE

m	N	E_t	Log A	t_+
0.01000	0.0199	+0.02294	0.87829	0.434
.01386	.0276	+ .01943	0.97493	.434
.01993	.0397	+ .01538	1.07555	.434
.02801	.0558	+ .01188	1.16909	.433
.03997	.0796	+ .00832	1.26174	.430
.05629	.112	+ .00508	1.34733	.424
.08114	.161	+ .00176	1.43632	.415
.1000	.199	.00000	1.48173	.408
.1378	.273	− .00264	1.55206	.395
.2026	.401	− .00529	1.63114	.371
.2724	.537	− .00714	1.68895	.343
.4069	.798	− .00915	1.75959	.290
.5444	1.06	− .01031	1.81164	.222
.8056	1.55	− .01132	1.88497	.115
.9996	1.91	− .01169	1.92480	.066
1.314	2.48	− .01178	1.97248	.015
1.896	3.49	− .01164	2.05843	− .068
3.0815	5.38	− .01000	2.18070	− .185

values. This is not surprising in view of the tendency of these salts to form complex ions. The values for cadmium iodide pass through zero at a concentration of about one-half normal.

The agreement for cadmium chloride is less satisfactory. Jahn's results for this salt cover the range from about 0.006 to 0.12 N and vary irregularly between 0.427 and 0.432, from which Noyes and Falk[5] give the constant value over this range of 0.430 in their table of "best values." Throughout this range the values here determined are much higher and, furthermore, pass through a minimum. Beyond 0.12 N they rise to a maximum, after which they fall continuously, passing through zero at about 7.4 N to negative values. If these inflection points are erroneous the values of the cation transference number from these results remain practically constant at about 0.480 up to about normal concentration, after which they decrease continuously. Although the deviation of the E_t-log A curve from a straight line is very slight, it seems nevertheless too great in view of the number of points determined in this region to attribute to experimental error. The peculiar variation of the transference numbers of cadmium chloride in dilute solutions may perhaps better be assigned to changes in the nature of the ionic complexes in this region.

It would appear from Jahn's values for cadmium bromide that at concentrations below those compared here the transference numbers may have had smaller values, indicating a minimum at low concentrations.

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[5] Noyes and Falk, THIS JOURNAL, 33, 1436 (1911).

Of this however it is impossible to be certain because of the small number of points and the experimental difficulties at high dilutions. In addition to this possible peculiarity of the transference numbers of the cadmium halides is the fact that all, as indicated above, pass to negative values at high concentrations. Again, while it is the general rule that values below 0.5 approach this quantity with increasing temperature, the results of Bein[6] on cadmium chloride would indicate that here too we find exceptional behavior, the values rising to markedly greater than 0.5.

Summary

Measurements at 25° of cadmium chloride and bromide concentration cells with liquid junction have been given at concentration ranges from 0.01 to 6 M and from 0.01 to 3 *M*, respectively.

From these data and the results from cells without liquid junction, the cation transference numbers of the salts have been calculated.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE PHYSICS DEPARTMENT OF THE JOHNS HOPKINS UNIVERSITY]

THE HEAT OF ADSORPTION OF GASES BY SOLIDS

BY K. F. HERZFELD

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Recently a number of measurements have been published for the heat of adsorption of gases by solids, showing a marked change of the heat with the amount of gas adsorbed. This change can be either a decrease[1] or an increase.[2] The first case can easily be explained by assuming the presence of spots with different affinity in the solid.[3] The spots with the higher affinity will adsorb the first part of the gas, and will in general give off larger amounts of heat.. To give a more detailed description of these sensitive spots Taylor[2,4] has pointed out that the surface of metals used in adsorption experiments is very rough. The atoms lying on the top of a small hill will be bound less strongly to their surroundings than the atoms in a flat surface. Accordingly they will have more of their chemical affinity left free to bind the atoms of the adsorbed gas in analogy to an idea familiar in organic chemistry. In the case of heteropolar salts as adsorbing substance, Kossel[5] has shown by direct calculation that the

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[6] Bein, *Z. physik. Chem.*, 27, 1 (1898).

[1] See F. Goldmann and M. Polanyi, *ibid.*, 132, 321 (1927).

[2] H. S. Taylor, *J. Plays. Chem.*, *30*, 145 (1926); G. B. Kistiakowsky, E. W. Flosdorf and H. S. Taylor, THIS JOURNAL, 49, 2200 (1927); W. E. Garner and D. McKie, *J. Chem. Soc.*, *2451* (1927).

[3] I. Langmuir, THIS JOURNAL, 38, 221 (1916); 39, 1848 (1917); 40, 1361 (1918).

[4] H. S. Taylor and G. B. Kistiakowsky, *Z. physik. Chem.*, 125,341 (1927).

[5] *W*. Kossel, *Gott. Nach.*, 135 (1927).

electric force on the surface of a crystal is rather weak for *a* flat surface, stronger in a place where a new molecular layer starts above a large flat surface, forming a step, and strongest in a place where a corner is formed, or where only one or two ions project out of a flat surface. Such an explanation cannot hold in the cases in which the heat of adsorption increases with increasing adsorption, because, as we have said before, if the change in the amount of heat is due to differences in the adsorbing spots, the adsorption will start in the spots where the energy difference is highest (at least if these energy differences are above a certain limit), as we shall discuss in the second part. A possible explanation of the increase can be found in the assumption that neighboring adsorbed molecules attract each other, because one sees easily that the number of places where two or more adsorbed molecules lie close together will increase relatively stronger with the amount of gas adsorbed than the number of places with isolated adsorbed molecules. One could argue that the mutual attraction of the molecules could not amount to more than the heat of evaporation of these molecules when present in a bulk of liquefied gas, and could accordingly not account for the actual increase in heat of adsorption, which is much higher, but this argument proves to be wrong on account of a fact pointed out by DeBoer.[6] If we assume the adsorbing forces to be of an electrical nature, the molecules will be polarized (this term being used now to mean as well the orientation of molecules carrying a permanent dipole as the displacement of charges inside the molecule, which is usually meant by this term). Now this polarization of the molecules will set up much stronger forces between them than in the absence of an external field, in the same way in which two rods of soft iron which do not attract each other appreciably outside of an external magnetic field act on each other strongly if magnetized by an outside source. In the first part of the paper we intend to discuss the amount of interaction which can be produced in this way; in the second part, we are going to discuss the relation between the amount of gas adsorbed and the heat of adsorption.

Interaction of Adsorbed Molecules[7]

If the idea discussed in the introduction is proved, then it turns out that even in the case mentioned first (of a decrease of the heat of adsorption with the amount of gas adsorbed) there might be another reason for it apart from the possibility that different spots have a different sensibility. For the sake of simplicity we are going to discuss the adsorption of a gas without permanent dipoles on the surface of a heteropolar salt—for example, the adsorption of hydrogen or oxygen on the surface of rock salt

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[6] J. H. DeBoer, *Physica*, [V] 8, 145 (1928).

[7] Similar ideas have been developed, although in less detail, by A. Magnus, *Z. Electrochem.*, 34, 531 (1928).

or fluorite. There will be then in general two types of spots on the surface which can adsorb, the positive and the negative ions of the lattice. Let us assume, for the sake of convenience. that one of these two will adsorb slightly more strongly than the other; for example, in the case of fluorite the calcium ions will adsorb more strongly than the fluorine ions on account of their double charge. Accordingly, first the calcium ions on the surface will be covered by adsorbed gas molecules. It might now happen that the size of the gas molecules is so large that no more gas molecules can be adsorbed between them on the fluorine ions even if we increase the gas pressure. Then, without interaction of the molecules, one would expect for a uniformly flat adsorbing surface no change in the heat of adsorption up to this saturation point; but, instead, we would get a decrease because now all adsorbed gas molecules are polarized in the same direction, all being adsorbed on ions of the same kind, and would, accordingly, repel each other, decreasing the heat of adsorption the nearer they get to each other, which means the more the surface is covered. If, on the other hand, the size of the gas molecules is such that it does not obstruct adsorption on neighboring ions of opposite sign, these adjacent gas molecules will be polarized in opposite directions, and will accordingly attract each other, increasing in this way the heat of adsorption.

Let us now assume that a molecule of the adsorbed gas gets, under the influence of an electric force E, a polarization p

$$p = \alpha E \tag{1}$$

a is connected with the dielectric constants of the gas under normal conditions, ϵ_0, and the number of molecules N_0 contained in one cubic centimeter under these conditions is by the formula

$$\epsilon_0 - 1 = 4\pi N_0 \alpha \tag{2}$$

The energy of an adsorbed gas molecule at 0 temperature taken negatively will then be, calculated for one mole

$$U_0 = N_L \frac{\alpha}{2} E^2 \tag{3}$$

where N_L is the number of molecules per mole. In this formula the molecules are supposed to be *so* far apart that they do not act on each other. On the other hand, if we have two molecules with the polarization p_1 and p_2 at the distance r, their mutual electrostatic energy will be

$$\pm \frac{p_1 p_2}{r^3} \tag{4}$$

with the $-$ sign in case of opposite polarization and the $+$ sign in case of polarization in the same direction. The outside fields are assumed to be parallel. They will be in general (at least approximately) at right angles to the surface, due to the symmetry at the positions of equilibrium for adsorbed molecules. If we now consider a pair of adjacent gas molecules adsorbed on two different spots suited for adsorption and situated close to each other, with the electric fields E_1 and E_2, their total energy will be (again taken with the negative sign)

$$\frac{U}{N_L} = p_1E_1 \pm \frac{p_1p_2}{r^3} + p_2E_2 - \frac{p_1^2}{2\alpha} = \frac{p_2^2}{2\alpha} \tag{5}$$

(+ sign for opposite polarization, − sign for same polarization)

Here the first and third members give the electrostatic work gained by generating the dipole p_1 in the electrostatic field E_1 (motion of a charge e over a distance l_1, $el_1 = p_1$) and the dipole p_2 in the field E_2. The fourth and fifth members am the elastic energy stored up in the distorted molecules, while the second member corresponds to the mutual electrostatic energy of the dipoles according to (4).

The strengths of the dipoles p_1 and p are such that they make the potential energy to a minimum, and are accordingly given by the equations

$$\frac{\partial}{\partial p_1}\frac{U}{N_L} = E_1 \pm \frac{p_2}{r^3} - \frac{p_1}{\alpha} = 0$$

$$\frac{\partial}{\partial p_2}\frac{U}{N_L} = E_2 \pm \frac{p_1}{r^3} - \frac{p_2}{\alpha} = 0$$

or

$$p_1 = \frac{\frac{E_1}{\alpha} \pm \frac{E_2}{r^3}}{\frac{1}{\alpha^2} - \frac{1}{r^6}} \qquad p_2 = \frac{\frac{E_2}{\alpha} \pm \frac{E_1}{r^3}}{\frac{1}{\alpha^2} - \frac{1}{r^6}} \tag{6}$$

From this we get the negative energy of the pair

$$\frac{U}{N_L} = \frac{p_1E_1}{2} + \frac{p_2E_2}{2} = \frac{1}{2}\,\frac{\frac{E_1^2 + E_2^2}{\alpha} \pm \frac{2E_1E_2}{r^3}}{\frac{1}{\alpha^2} - \frac{1}{r^6}} \tag{7}$$

In the simplest case we put $E_1 = E_2$. This will hold either if the molecules are adsorbed only by a single kind of ion (negative sign, repulsion), or if the adsorbing power of both ions is about equal, as in potassium chloride, and the size of the molecules so that they can be adsorbed by neighboring ions. Then we get as energy per mole (not per pair of moles)

$$U = \frac{N_L}{2}\,\frac{F_1^2}{\frac{1}{a} - \frac{1}{r^3}} = \frac{N_L\alpha F^2}{2}\,\frac{1}{1 \mp \frac{a}{r^3}} \tag{8}$$

α and r^3 being referred to one molecule are cumbersome numbers. We introduce instead the numbers referring to 1 mole by multiplying with N_L in numerator and denominator of the fraction α/r^3, and use the equation in the form

$$U = \frac{N_L\alpha\, E^S}{2}\,\frac{1}{1 \mp \frac{N_L\alpha}{N_Lr^3}} \tag{8'}$$

The second factor gives the relative change of the heat of adsorption. To evaluate this numerically, we proceed in the following way. According to Equation 2

$$N_L\alpha = \frac{22,400}{4\pi}(\epsilon_0 - 1) \qquad (2')$$

where 22,400 is the number of cc. in a mole of a gas under normal conditions. The units in (1') are cc. The following table gives some examples

Gas......	H_2	O_2	N_2	CO	CH_4	C_6H_6
$N_L\alpha$......	0.55	0.80	1.13	1.28	1.70	6.04

On the other hand, N_Lr^3 can be calculated as follows.

If we have adsorption on each ion of a rock salt lattice, N_Lr^3 will be the volume of 1 mole of ions, or half the mole volume of the salt. If adsorption takes place only on positive ions, N_Lr^a will be four times the mole volume.

If we consider the adsorption on a metal to be of a similar nature[8] (see later), adsorption at the places where atoms sit will result in repulsion of the adsorbed molecules (positive sign). However, for a face-centered lattice like copper we would have to use half the molecular volume if we assume molecules to be adsorbed by positive ions in the lattice points, and molecules with opposite polarization adsorbed between them by electrons distributed uniformly in the space between the ions. If, on the other hand, adsorption could occur only at the lattice points occupied by metal atoms, the volume would have to be twice the molecular volume. The next table shows some examples.

	Adsorption on same kind of ions only (Repulsion between adsorbed molecules)			**Adsorption on both kinds of spots (Attraction between adsorbed molecules)**		
Substance......	NaCl	**Cu**	**Pt**	NaCl	**Cu**	**Pt**
N_Lr^3..........	107.6	10.05	12.9	13.5	3.56	4.56

Calculation of (8) from the data in the two tables shows that the mutual repulsion in the first case (repulsion) could not change the heat of adsorption appreciably for a salt, and might change it by about 10% on a metal in the case of small gas molecules. On the other hand, attraction between adsorbed molecules will increase the heat of adsorption by about 10% on salts and up to 40 or 50% on metals (again for simple molecules). This number will be made somewhat larger if not only pairs but groups of more molecules are formed. For example, if there is a group of three molecules, one adsorbed by a sodium ion and two on opposite sides of it, each adsorbed by a chlorine ion, the influence is increased by a factor of about 4/3.

We have computed this change only relative to the electrostatic part of the energy of adsorption. Compared with the total energy of adsorption this fraction might be less if a large part of the energy of adsorption is due to Van der Waals forces, as Lennard-Jones[9] suggests. On the other

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[8] H. S. Taylor, "Colloid Symposium Monograph," Vol. IV, 1926, p. 19.

[9] J. E. Lennard-Jones and Beryl M. Dent, *Trans. Faraday Soc.*, **24**, 92 (1928).

hand, it might be more if in the total heat of adsorption there is present a large negative part due to the forces of repulsion which act between the gas molecules and the adsorbing solid, and fix the position of equilibrium of the adsorbed gas molecules. These latter forces might play a more important part here than in the lattice energy of heteropolar crystals, because the force of attraction in adsorption changes more strongly with the distance than the inverse second power;[9] but, in any case, it seems that for the adsorption of carbon monoxide on copper,[2] one would not expect the rise to more than the double value.

We have to justify now our assumption that the adsorption forces in the case of metals are of the same nature as those in heteropolar salts. The newer development of the electron theory by Sommerfeld[10] has removed the difficulties which adhered to the older form of the theory, and has again made reasonable the old assumption that a metal is built up as a lattice of positive ions with the free electrons distributed approximately uniformly[11] between them. In this case there will be an electrostatic field on the surface of the metal of a type very similar to the one on the surface of a crystal like rock salt. However, it seems somewhat doubtful to the author whether the same idea can be applied to carbon (charcoal). If so, in this case the distance between neighboring atoms is $1.5 \cdot 10^{-8}$ cm., and the repulsing forces due to adsorbed molecules polarized in the same direction would require the introduction of 2.04 cc. as the value for $N_L r^3$ in (8), giving a very strong decrease of the heat of adsorption with the amount of gas adsorbed. If, on the other hand, adsorption on spots of opposite character could be possible, this could not be in the middle of the line between two atoms of carbon on account of the short distance but would have to be in the center of the ring formed by each group of six atoms in graphite. In this case the number to be inserted in (8) would have to be ~ 2 cc. To account in this way for the curve given by Polanyi[1] one would, therefore, explain the initial decrease of the heat of adsorption as due to the fact that gradually less sensitive spots come into action. The increase after the minimum would be due to the formation of pairs or larger groups with mutual attraction. The final sharp maximum with corresponding quick fall might mean the covering of much less sensitive places.

Thermodynamic Consideration of the Increase in the Heat of Adsorption.—The foregoing discussion might alleviate a difficulty which seems connected with the experimental result that the heat of adsorption increases. From the thermodynamical standpoint it is clear that the processes which will first take place are the ones where the decrease in free

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[10] A. Sommerfeld, *Z. Physik*, *47*, 1 (1928).

[11] H. Bethe, *Ann. Physik*, *87*, 55 (1928); J. E. Lennard-Jones and H. J. Woods, *Proc. Roy. Soc. London*, 120,727 (1928).

energy is largest, while the experiment shows that at the same time the decrease in total energy is relatively small, and will be much larger for later processes of adsorption. This difficulty has been pointed out by the author to Dr. Kistiakowsky and Dr. Taylor, and has been mentioned by them.[2] R. E. Burk,[12] in his recent report on contact catalysis, states that it is perfectly possible that a large change in free energy is connected with a small change in total energy due to a large difference in the chemical constants. While this is quite true in principle, the difficulty in the present case rests just on the numerical values which seem possible from a kinetical standpoint, and it might be of interest to discuss the question here in general.

In any physical or chemical equilibrium the probability that a molecule will be in a certain state is proportional to[13]

$$ve^{+U/RT} \tag{9}$$

Here U is the negative potential energy in this state calculated for 1 mole, while v is the "average available volume" in the phase space which belongs to this state. Here we have assumed that the classical theory holds, the temperature being high enough to insure equipartition for the kinetic energy.

v is a product, each factor belonging to one degree of freedom. The connection between (9) and the free energy, p, is given by

$$e^{-\mu/RT} \sim ve^{+U/RT} \tag{9'}$$

where μ is the free energy of the system per mole. Some additional members referring to the kinetic energy are left out due to the fact that we have left out the corresponding factors in v. If we now want absorption to occur first at places with smaller heat of adsorption $(+$ U), these places must have a correspondingly higher v. If the logarithm of (9') is taken this statement is equivalent to the usual statement that a small change of the total energy might be overcompensated by a large change in the chemical constants (or the specific heats). To compensate for an increase in the heat of adsorption, there must be a factor 10 in v for each increase of about 1400 calories at room temperature, as $e^{-1400/RT}$ is about $^1/_{10}$th. We have therefore to discuss next the factor v.

(A).—When a gaseous molecule is bound, the three degrees of freedom of translation go over into three degrees of oscillation around the position of equilibrium. The corresponding factors in v are

$$\left(\frac{1}{\nu}\sqrt{\frac{kT}{2\pi m}}\right)^3 \tag{10}$$

Accordingly, for a given gas these factors are in the ratio ν_2^3/ν_1^3 for two different positions. From our knowledge of infra-red vibration it would

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[12] R. E. Burk, *J. Phys. Chem.*, **32**, 1601 (1928).

[13] K. F. Herzfeld, *Physik. Z.*, **22**, 186 (1921); **23**, 95 (1922); "Kinetische Theorie der Wärme," Braunschweig, 1925.

seem improbable that the ratio of frequency for different positions could be larger than 2:1. A similar conclusion can be reached if we assumed that the potential energy of the molecule is given by an expression like $\frac{A}{r^m} - \frac{B}{r^n} = U$. A simple calculation shows that the frequency is given by

$$4\pi^2 M\nu^2 = \frac{mn}{r^2} U$$

This formula also makes it improbable that for a given substance the frequency might vary more than two-fold. This means that these three degrees of freedom could, at the utmost, be responsible for a change in v by a factor 8, which would compensate an energy difference of 1250 calories. (As in general the higher energy will correspond to a higher frequency, the change in v is in the right direction.)

(B) Internal Vibrations.—Burk suggests that the internal vibration of the molecule might be affected. Considering the strength of the internal forces compared with the strength of the adsorption forces, it seems improbable that the change in frequency of the internal vibration would be more than, let us say, 12%. Each internal degree of freedom will produce a factor similar to one of the three factors in (10). Accordingly, one would expect at the utmost compensation for 60 calories for each internal degree of freedom. The same will be true for an influence upon the vibration of the molecules of the adsorbing solid. It seems to the author, therefore, that this part can be neglected.

(C) Rotations.—If we have to deal with a gas molecule which is not monatomic, this gas molecule will have rotational degrees of freedom, two in number for a diatomic molecule or a straight molecule like carbon dioxide, three for all other molecules. For the adsorbed molecule it might be that on all spots adsorbing these rotations will be changed into oscillations of the axis of the molecule around an equilibrium direction. In this case we get in v again factors of the form (10). There will be two of them. for a straight molecule, three for a more complicated one. This will mean for the ratio of the two v's for two different spots a ratio of $(\nu_2/\nu_1)^2$ or $(\nu_2/\nu_1)^3$. In numbers this might make a factor of four or eight, if we assume again that the frequencies cannot be changed more than by a factor of two. Accordingly, this might compensate for 800 or 1250 calories. We might get a stronger effect if we assume that in one of the spots the molecule might turn freely, while in the other one it might only be allowed to oscillate. For example, it might be that on adsorption at a flat plane a molecule might turn freely around an axis perpendicular to this plane, while if adsorbed in a corner and accordingly fixed by more than one spot it might be forced to oscillate only.

To make an estimate for this case, consider a permanent dipole in a homogeneous electric field, E. This dipole will either rotate or oscillate around the field according to the strength of the field. A short calculation shows that Expression 9' takes the form

$$v_0 \frac{kT}{pE}\left(e^{+pE/kT} - e^{-pE/kT}\right)$$

where v_0 is the value of v for the rotation of a free molecule and p is the moment of the permanent dipole. If pE, the amount of potential energy at absolute zero, is sufficiently large compared with kT, this takes the form

$$v_0 \frac{kT}{pE} e^{U/RT}$$

showing that here we have in fact a factor kT/pE smaller than that appearing before the e-power with the larger energy. This formula is essentially no different from the formula just mentioned above because we have to deal here with vibrations around a given axis in two dimensions, in which case, according to our previous reasoning, we should have a factor proportional to $(\nu_2/\nu_1)^2$ and, on the other hand, pE is proportional to $\sim v^2$. But the factor which we find here cannot be much smaller than $^1/_{10}$th (corresponding to $NpE \sim 6000$ small calories), and would accordingly compensate for about 1400 small calories (for half this amount, if there were only one degree of freedom; for 1.5 the amount if there were all three degrees of freedom of rotation).

(D) A Majority of Spots with Low Heat of Absorption.—If we assume that there are two kinds of spots, one with a low heat of absorption, U_1 (number of these spots per square centimeter, N_1), and one with high heat of absorption, U_2 (number of these spots per square centimeter, N_2), we will get for the ratio of molecules adsorbed on these two kinds (n_1, n_2) if we make assumptions similar to Langmuir's

$$\frac{n_2}{N_2 - n_2} = \frac{n_1}{N_1 - n_1}\frac{v_2}{v_1} e^{(U_2 - U_1)/RT} \tag{11}$$

We call $n = n_1 + n_2$ the total number of molecules adsorbed and introduce the abbreviation

$$A = \frac{v_2 N_2}{v_1 N_1} e^{(U_2 - U_1)/RT} \tag{12}$$

Then a rather complicated calculation shows that the (differential) heat of adsorption will be given by

$$U_1 + (U_2 - U_1)\frac{1}{1 + \dfrac{AN_1N_2}{[(1-A)n_2 + AN_2]^2}} \tag{13}$$

The slope of this curve is shown to be

$$\frac{(U_2 - U_1)\, 2N_1N_2A(1-A)}{\left[(1-A)n_2 + AN_2 + \dfrac{AN_1N_2}{(1-A)n_2 + AN_2}\right]^3} \tag{13'}$$

Accordingly this expression will have the sign of $1 - A$, and will be positive (rising heat of adsorption) if A is smaller than 1, which means that the larger heat of adsorption of spots No. 2 can be compensated not only by a smaller volume v_2 but also by a smaller number of spots N_2. But if this is so, then the resulting curve will not have the form given by Taylor and Kistiakowsky,[2] because if one calculates now the next differential quotient, which measures the curvature of the line, it turns out to be given by the following expression, which appears multiplied with essentially positive factors (even powers)

$$(U_2 - U_1)\,\frac{A\,\frac{N_1}{N_2} - \left[A\left(1 - \frac{n_2}{N_2}\right) + \frac{n_2}{N_2}\right]^2}{A\left(1 - \frac{n_2}{N_2}\right) + \frac{n_2}{N_2}}$$

A discussion of this expression shows that with A smaller than 1 this expression is positive, which means a line curving upward, while in the experimental curve the slope is steadily decreasing with an increase in the amount adsorbed. It is not quite out of the question that such a form could be explained if we assume more than two different kinds of spots present,[14] but from the present assumption it would follow that N_1 large compared with N_2 does not explain the experimental facts.

(E) Formation of **Pairs.**[15]—We consider, now the effect of the attraction between two neighboring molecules. To simplify the formulas we assume that there will always be two adjoining spots on the adsorbent at which adsorption might take place. For example, in the case of a heteropolar salt as adsorbent there might be always pairs of ions sticking out scattered over a plane surface. We call N the number of these double spots per square centimeter, n the total number of adsorbed gas molecules per square centimeter, n_2 the number of pairs, and n_1 the number of adsorbed gas molecules occupying alone a spot which could hold two. We have, therefore, $n = n_1 + 2n_2$. Furthermore, we use the abbreviation

$$B = 4\,\frac{v_2}{v_1}\,e^{(U_2 - U_1)/RT} \tag{14}$$

We now compare the probabilities that a newly adsorbed molecule will either form a pair with one already adsorbed or will stay single. In the first case it will have to go in an empty place, the neighbor of which con-

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[14] In fact, Kistiakowsky's calculations can be formally explained in this way. He gets a curve of the appropriate form by writing for the heat of adsorption

$$\Sigma_j N_j\,\frac{(W_j - w)\,e^{W_j/RT}}{1 + n^r k_j\,e^{W_j/RT}} : \;\Sigma_j\,\frac{N_j\,e^{W_j/RT}}{1 + n^r k_j\,e^{W_j/RT}}$$

If we write now $W_j - w = N_j$, $e^{W_j/RT} = v_j\,e^{U_j/RT}$, $v_j = e^{W/RT}\,k_j$, $N_j' = N_j/k_j$. This can be put into the form

$$\Sigma_j U_j\,\frac{N_j' v_j\,e^{U_j/RT}}{1 + n^r v_j\,e^{U_j/RT}} : \;\Sigma_j\,\frac{N_j' v_j\,e^{U_j/RT}}{1 + n^r v_j\,e^{U_j/RT}}$$

but then we have again the difficulty of explaining the large differences in the v's which would be given by the expression $v_j = k_j\,e^{W/RT}$.

[15] See also J. Frenkel, *Z. Physik*, 26,117 (1924).

tains already one adsorbed molecule. There are n_1 such places per square centimeter. On the other hand, if it should stay single it will have to go to a spot formed by two ions on which there is not yet any adsorbed molecule. There are $N - n_1 - n_2$ such spots. We get, therefore, the equation of our adsorption isotherm

$$\frac{n_2}{n_1} = \frac{n_1}{N - n_1 - n_2}\frac{B}{4} \tag{15}$$

Eliminating n_2 and calling the fraction x, which gives the amount adsorbed in terms of the saturation amount, $x = n/2N$, a short calculation gives the formula

$$n_1 = \frac{N}{B-1}\left(\sqrt{(B-1)4x(1-x)+1} - 1\right) \tag{16}$$

From this we get for the differential heat of adsorption

$$U_2 - (U_2 - U_1)\frac{1-2x}{\sqrt{(B-1)4x(1-x)+1}} \tag{17}$$

From this it follows that for a very small amount adsorbed (x negligible) the differential heat of adsorption will be U_1, as in this case all molecules will be single. With increasing amount adsorbed the relative amount of pairs will increase. For x very small the formula will be $U_1 + (U_2 - U_1)2Bx$, giving an increase in heat of adsorption. If B is comparatively large, we will have in the middle part of the range (x neither too small nor too close to 1) approximately the formula

$$U_2 - (U_2 - U_1)\frac{1-2x}{2\sqrt{Bx(1-x)}}$$

Finally, at the upper end, when $1 - x$ is very small, we get $U_2 + (U_2 - U_1)$ $2B(1 - x)$, a final linear increase ending up with a value $2U_2 - U_1$. The final differential heat of adsorption is much larger than half the heat of adsorption of one pair ($^1/_2\ 2U_2$) because, if we form one pair by adding one molecule at a place where another sits, we get not only the heat of adsorption U_2 of the newly added molecules, but we increase also the heat U_1 of the first molecule to U_2. (This is the same thing Polanyi[1] calls the heat of compression developed in the substance already adsorbed by further adsorption.) Roughly the curve which gives the heat of adsorption as a function of the amount adsorbed would look like Fig. 1. Unfortunately, it seems difficult to get this into agreement with the first part of the experimental curve. If we assume that U_1 is 5000 cal., and $U_2 - U_1 = 6000$ cal., we

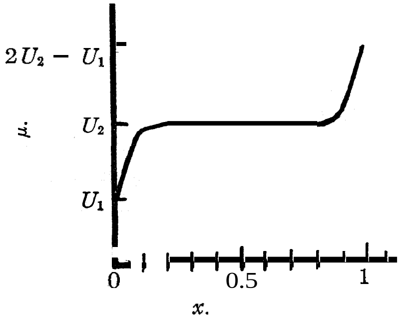

Fig. 1.—Heat of adsorption depending on the amount of gas adsorbed, if there is formation of pairs of molecules or dissociation.

have adjusted starting and end-point to the values 5000 and 17,000. Prom what we have seen before, this will make B = 400 even if we make v_1/v_2 equal to 100, which is the best we can do. This will give us for $x = {}^1/_{10}$th the differential heat of adsorption 10,600, and for $x = {}^9/_{10}$th, the value 11,400. In other words, there will be a very steep rise from 5000 to 10,600 during the adsorption of the first tenth of the gas; then only a rise of 800 more calories during the next ${}^8/_{10}$ths, and finally again a steep rise of 5600 calories during the last tenth of adsorption. The only way in which this could be smoothed out would be to make B smaller, but this would again necessitate making v_2/v_1 smaller, and as stated before there seems to be no way to do it. The decrease of the heat of adsorption beyond the maximum will, in any case, have to be explained by the presence of a different kind of adsorption spots, which are not included in N and which might be the spots on the plane surface. The inclusion of these in a way similar to (D) or to Kistiakowsky[14] might make somewhat smoother transitions in the first part of the curve, but would probably necessitate a higher value for $U_2 - U_1$, offsetting this advantage.

(F) Dissociation.—We have finally to consider the possibility advocated by Taylor and Kistiakowsky that on the spots with the lower heat of adsorption the molecules might be dissociated (into atoms for diatomic molecules, into other parts for larger molecules). In this case the lower heat of adsorption would be due to the energy necessary to dissociate the adsorbed molecule. If we again call N the number of available spots, assume furthermore that such a spot can be occupied either by a molecule (number n_2), or an atom (number n_1) we get the following equations for the adsorption

$$n_2 + \frac{n_1}{2} = n \quad \text{and} \quad \frac{n_2}{N - n_2 - n_1} - \frac{n_1^2}{(N - n_2 - n_1)^2}\frac{C}{4} \tag{18}$$

where C is an abbreviation for

$$C = 4\,\frac{v_2}{v_1^2}\,e^{(U_2 - U_1)/RT} \tag{19}$$

Here v_1 is the corresponding volume for one adsorbed atom; accordingly, v_1^2 is the volume for both atoms, U_1 is the heat developed by adsorption and subsequent dissociation into two atoms. If we again call x the ratio of the total amount adsorbed to the saturation amount $\left(\text{this time } x = \frac{n}{N}\right)$, we again get Equation 16, only with C instead of B. In the same way we get for the differential heat of adsorption, Equation 17 with C instead of B, and all of the subsequent discussion remains unchanged. The only task left is to discuss the numerical value of C, which amounts to discussing the ratio v_2/v_1^2. Now, as we said before, we can divide v_2 into two factors, $v_2 = v_2'v_2''$. Here v_2' is due to the oscillation of the molecule as a whole around its position of equilibrium, and accordingly the discussion under (A) applies. It follows that if we write for v_2/v_1^2 the expression v_2'/v_1 X v_2''/v_1, the first factor will be 8 to 10 at the best.[16] v_2'', on the other hand, is due to the motions of the adsorbed molecules around a certain direction, as stated in (C), and this motion might either be an oscillation or a free rotation. In the first case the ratio will be $(\nu_1/\nu_2)^3$, or again a factor of 10 at the best. In the latter case we get for this ratio $8\pi^2\nu_1^2I/kT$, where **I** is the moment of inertia. With a frequency of $\nu_1 = 10^{13}$ (wave length, 30μ), and a moment of inertia of 10^{-40}, this would make a factor 20, with a wave length of 100μ ($\nu_1 = 3 \times 10^{12}$) and $\mathbf{I} = 10^{-41}$, as in the case of hydrogen, the value would be 0.2. So it seems impossible to expect for v_2/v_1 anything smaller than 0.01, but probably the value will he much larger; accordingly for the same difference $U_2 - U_1$ measured experimentally, C will be at least as large as B. Accordingly, the interpretation of the effect as dissociation into atoms will lead to even greater difficulties than the assumption of formation of pairs discussed under (E).

Thermodynamical Comparison of Two Gases with the Same Heat of Adsorption

From what we have said before it will now be easy to answer the question under what conditions the amount of gas adsorbed on the same adsorbent under the same external pressure will be different for two gases with approximately the same heat of adsorption, or in other words, comparing the two gases when the same amounts are adsorbed, under which conditions the equilibrium pressure will be different. The equilibrium pressure will be inversely proportional to the expression (9'). If we have the same U, it will be inversely proportional to v. First of all, as far as the vibrations of the molecule, as a whole, are concerned (A of the preceding part), it is merely a question of how different the forces can be for the same energy; here, too, we might assume that these forces will surely not vary more than the ratio 1:4, giving at the utmost the factor 8. As far as the influences are concerned which are mentioned in (C), it seems possible that if one molecule is rotating freely, and the other one only oscillating around one direction, the latter might have a vapor pressure 20 times as great as the former. It might be that if we compare a mole-

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[16] **Here the ratio is not really $(v_1/v_2)^3$ because the two things compared have not the same masses, but is $(m_1v_1^2/m_2v_2^2)^{3/2}$, or the ratio of the quasi-elastic forces to the third power, which is really the expression to which our discussion applies, but probably in this case it will be $m_1v_1^2$ which will be greater than $m_2v_2^2$, because the forces which bind the atom to the adsorbent are greater than the forces which bind the molecule, in spite of the fact that U_2 is larger than U_1. U_1 is not the heat liberated if we adsorb two atoms out of the gaseous state, but the heat liberated if we first adsorb a molecule and then dissociate it in the adsorbed state. For a detailed discussion see, for example, M. Polanyi, *Z. Elektrochem.*, 27, *142 (1921)*. From what we have said before it is more probable that v_2'/v_1 is 10 than $^1/_{10}$th.**

cule without permanent dipole, like H_2, with a molecule with permanent dipole, like H_2O, these conclusions might apply. Finally, if we compare molecules which dissociate with molecules which do not and adsorb only very small amounts, we might expect for the dissociating molecules a vapor pressure lower than that for the non-dissociating. This follows in the manner shown. The vapor pressure p_1 of the first kind will be proportional to $(n_1^2/N^2)v_1^2e^{(U_1/RT)}$ if so little is adsorbed that practically all is dissociated and only a small part of the surface covered. On the other hand, the vapor pressure of the non-dissociating type, p_2, will be proportional to $(n_2/N)v_2e^{(U_2/RT)}$. If, then, $U_1 = U_2$, and the same amount of moles, $n = n_2 = 2n_1$, is adsorbed, we find

$$\frac{p_1}{p_2} = \frac{n}{4N}\frac{v_1^2}{v_2}$$

The latter factor has been discussed in the last section of the preceding part while the first factor is small compared with one and proportional to the amount adsorbed.

Summary

In the first part it is shown that the increase in heat of adsorption with the amount of gas adsorbed can be explained by the interaction of the dipoles in neighboring molecules which are set up if we assume that the adsorption is mainly due to electric forces. In this case the interaction can be much stronger than the usual heat of evaporation would lead us to expect.

In the second part the thermodynamical difficulty connected with an increase in heat of adsorption is discussed. It is shown that the best explanation seems to be the formation of groups of adsorbed molecules sticking together.

Finally, the equilibrium pressures of different gases with the same heat of adsorption are compared.

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ACTIVITY COEFFICIENTS OF ELECTROLYTES. III. THE PRINCIPLE OF SPECIFIC INTERACTION IN MIXTURES OF HIGH VALENCE ELECTROLYTES[1]

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1. Introduction

One of the most promising attempts to account for the specific deviations from the laws of uniform behavior of given valence type which individual strong electrolytes exhibit at concentrations other than those of extreme dilution, was presented by Bronsted[2] in a paper entitled "The Principle of Specific Interaction of Ions," published previous to the appearance of the theory of Debye and Hückel.[3] The purpose of this investigation was to subject this principle to *a* more extended test by studying mixtures of higher valence types of salts than in previous tests, in order to determine its limits of applicability. The fundamental physical assumption of the principle of specific interaction is that those specific effects which are due to electric forces should occur only between ions of *opposite* sign, since they approach each other closely while the electrical interaction between ions of *like* sign may be considered uniform, since on the average these ions are far apart.

This postulate may be expressed as follows.[2,3] If we let A_1B and A_2B represent two solvent salts with an anion in common (B), and having the same *equivalent* concentration, and let X represent an arbitrary cation and Y an arbitrary anion, present in small amount in the two solvents, then

$$\frac{f_{X(A_1B)}}{f_{X(A_2B)}} = F\ (A_1, A_2) \tag{1a}$$

and

$$\frac{f_{Y(A_1B)}}{f_{Y(A_2B)}} = F\ (A_1, A_2, Y) \tag{2a}$$

That is, the *ratio of the activity coefficients*, f, of the same cation in two equally strong solutions having an anion in common is a *function* only *of the nature of the two cations of the solvents;* the ratio of the activity coefficients of the same anion in two equally strong solutions having an anion in common is a function of the nature of the cation considered and the cations

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[1] The material for this paper is constructed from a dissertation submitted by R. Graham Cook to the Faculty of Pure Science, Columbia University, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, May, 1928. An abstract was presented before the Division cf Physical and Inorganic Chemistry at the Swampscott (September, 1928) Meeting of the American Chemical Society.

[2] Brönsted (a) THIS JOURNAL, 44,877 (1922); (b) 45,2898 (1923).

[3] For a review and summary see La Mer, Trans. *Am. Electrochem. Soc.,* 50, 631 (1927).

of the two solvents. By equally strong solutions here is meant solutions of the same *equivalent* concentration, that is, where the total number of charges, irrespective of sign, is the same in each solution.

When solvents of the type AB_1 and AB_2, where the cation is common, are employed, Equations 1a and 2a become

$$\frac{f_{X(AB_1)}}{f_{X(AB_2)}} = F(B_1, B_2, X) \tag{1b}$$

$$\frac{f_{Y(AB_1)}}{f_{Y(AB_2)}} = F(B_1, B_2) \tag{2b}$$

As a result of these equations we should have the follo ing solubility relations, when we take AgCl, AgBr and TlCl as simple examples of uni-univalent saturating salts for purposes of illustration, and KNO_3, $NaNO_3$, $NaClO_3$, etc., to represent the aqueous solvents in which they are dissolved, namely,

$$\frac{S_{AgCl(KNO_3)}}{S_{AgCl(NaNO_3)}} = \frac{S_{AgCl(KClO_3)}}{S_{AgCl(NaClO_3)}} = \frac{S_{TlCl(KNO_3)}}{S_{TlCl(NaNO_3)}} = --- \tag{3}$$

and similarly when the terms cations and anion are interchanged

$$\frac{S_{AgCl(KNO_3)}}{S_{AgCl(KClO_3)}} = \frac{S_{AgCl(NaNO_3)}}{S_{AgCl(NaClO_3)}} = \frac{S_{AgBr(KNO_3)}}{S_{AgBr(KClO_3)}} \tag{4}$$

2. Plan of the Investigation

Although considerable experimental data[2,4] have been accumulated in support of the theory, the evidence has been confined to the use of solvent salts of the simple uni-univalent type, with the exception of an important series of measurements[2b] involving Na_2SO_4 and NaCl as the solvents for two $(1, -1)$ and two $(1, -2)$ types of saturating salts having the ion $[Co(NH_3)_4C_2O_4]^+$ as cation.

In no case have any of the tests involved solubility data where the ions of opposite sign in the solute and solvent salts (*i. e.*, X and B, and Y and A) were both of a valence higher than unity. Such a test is of particular interest since La Mer and Mason[5] found extremely marked deviations from the Debye limiting law under these conditions even at very high dilutions. They found entirely normal results for the solubility of **(3, — 1)** salts involving the luteo cobaltic cation in the presence of solvent salts containing univalent anions, but when they employed sulfate solvents, the experimental curve for $-\log f$, when plotted against the square root of the ionic strength, gave no evidence of fusing into the limiting law of Debye and Huckel. If it can be shown that the principle of specific interaction holds at 0.1 N concentrations for these salts, then one should have little fear in applying it to mixtures which obey the present form of Debye theory.

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[4] Güntelberg, Z. *physik.* Chem., 123, 199 (1926).

[5] La Mer and Mason, THIS JOURNAL, 49, **363** (1927). See also the next paper of this series, *ibid.*, 51, 2632 (1929), where the same behavior is found for $La(IO_3)_3$.

Because of the important theoretical significance of this result, we first repeated La Mer and Mason's measurements at low concentrations on independently and freshly prepared salts (Parts 5 and 6). It also seemed desirable to determine whether or not the solubility ratios, when B_1 and B_2 were of different valence, retained the same numerical value when the common solvent cation A was changed in valence; and similarly when the common anion B was changed in valence and the solvents cations A_1 and B_2 are of different valence. If the equivalent concentration is the appropriate scale for comparisons regardless of the valence type of solvent, then no change should occur in these cases. Such a result, however, would conflict with the Debye-Hückel theory, for this theory predicts that the contribution due to primary Milner effect (ideal value dependent only on valence type and independent of specific properties) is proportional to the ionic strength and not to the equivalent concentration.

We should expect, therefore, to obtain constant ratios only when the ratios of the ionic strengths of the solvents remain unchanged at the same equivalent concentration. This proves to be the case.[6]

3. Experimental

The saturating salts employed in this investigation were (1) luteo-cobaltic di-ammino tetra-nitro cobaltiate, $Co(NH_3)_6[Co(NH_3)_2(NO_2)_4]_3$, which we shall represent hereafter by the symbol "LN₃" (S_0, the solubility in moles per liter in pure water, is 1.64 X 10^{-4}); (2) luteo-cobaltic di-ammino di-nitro oxalo cobaltiate, $Co(NH_3)_6[Co(NH_3)_2(NO_2)_2C_2O_4]_3$, symbol, "LOn₃" ($S_0 = 0.826 \times 10^{-4}$); (3) luteo-cobaltic ferricyanide, $Co(NH_3)_6Fe(CN)_6$, symbol, "LF" ($S_0 = 0.30 \times 10^{-4}$); and (4) luteo-cobaltic cobalticyanide, $Co(NH_3)_6Co(CN)_6$, symbol, "LC" ($S_0 = 0.22 \times 10^{-4}$). The first two, the tri-univalent salts, were employed in that part of the investigation where the conclusions of La Mer and Mason[4] were to be tested. All four were used as saturating salts for the experimental test of the specific interaction theory. The LN_3 salt became so soluble in tenth normal salt solutions that it was not possible to run a whole series of measurements on the same sample of saturating salt, and only a few measurements were made on this salt. On the other hand, it was possible to measure the solubility of the LOn_3 salt in a complete series of solvent salts, using the same sample throughout.

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[6] Brönsted, ref. 2b, p. 2908 recognized the error in assuming that the primary Milner effect is determined by the equivalent concentration, but since he finds, p. 2909, "that the identity of values found by comparing two isotopic salts with a common cation appears only when the equivalent concentration is used" and "not at the same molar concentration or ionic strength"—a conclusion which our data also support (see data for $TlIO_3$ in the following paper)—it seemed desirable to obtain data bearing on this point in hopes of discovering an appropriate scale or scales for purposes of camparison. As far as we are aware no data bearing on this question have been presented.

The method used and the various precautions to be observed in carrying out the solubility determinations have been described in detail previously.[7] The original thesis should be consulted for further details concerning these measurements.

4. Preparation of Materials

Luteo-cobaltic Nitrate.—This salt was prepared by the iodine method of Biltz[8] and recrystallized from dilute nitric acid, washed with water containing a little nitric acid and finally thoroughly washed with 95% ethyl alcohol. It was dried in the oven at 100°.

Ammonium **Di-ammino** Tetra-nitro **Cobaltiate.**—The method given by Jdrgensen[9] was followed. The salt was twice recrystallized from water and allowed to dry spontaneously.

Ammonium **Di-ammino** Di-nitro Oxalo **Cobaltiate.**—This salt was obtained by adding to a solution of the above salt a solution of oxalic acid, in the correct molecular proportions according to the direction of Jörgensen.[10] It was once recrystallized from water. The luteo-cobaltic saturating salts were prepared from the above salts by methods previously described.[5,11]

Salts of Potassium and **Sodium.**—Potassium nitrate, potassium chloride, potassium sulfate, sodium chloride, sodium nitrate and sodium sulfate: the best "C. P." grades obtainable were twice recrystallized from redistilled water, dried in the oven at 120°, ground in an agate mortar and dried again at 120° for twenty-four hours.

Salts of Magnesium—Concentrated solutions of all salts gave no qualitative tests for calcium, barium, strontium, sodium, potassium or ammonium ions as impurities, except magnesium chloride, which contained very small amounts of ammonia, as described later.

Magnesium Sulfate.—A "C. P." product was twice recrystallized, dried in the oven at 50° for three days, then kept in a desiccator over phosphorus pentoxide for a week. The "apparent" molecular weight of the hydrate was determined by igniting a weighed sample to constant weight in a crucible, thus determining the magnesium as magnesium oxide. It was kept in a glass-stoppered bottle sealed with paraffin.

Magnesium Chloride.—Of all the solvent salts employed, this was the only one which was found to contain ammonium salts in appreciable amounts. A sample of Kahlbaum's "zur Analyse" grade was found to have the least amount of ammonia present. A 100-cc. aliquot of 0.1 N $MgCl_2$ solution contained ammonia equivalent to 0.15 cc. of 0.02073 N HCl. Thus one liter of the salt solution would contain only 0.5 mg. of NH_3. A stock solution of the $MgCl_2$ was made up, the chloride determined by titrating against 0.1034 N silver nitrate solution (Mohr method), and the solution diluted to 0.1000 N and re-checked against the silver nitrate solution before use.

Lanthanum Salts.—Samples of the hydrated salts were obtained from the Welsbach Company, who especially purified the salts to free them from cerium and other rare earths. Tests for cerium by the sensitive hypochlorite method[12] gave negative results.

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[7] La Mer, King and Mason, THIS JOURNAL, 49,363 (1927).

[8] Biltz, "Laboratory Methods of Inorganic Chemistry," John Wiley and Sons, Inc., New York, 1909, p. 176.

[9] Jorgenson, Z. *anorg.* Chem., 17, 476 (1898). See also Thomas, "Complex Salts," Blackie and Son, Ltd., Glasgow, 1924, p. 116.

[10] Jorgensen, *Z. anorg. Chem.*, 11,445 (1896).

[11] Jorgensen, *ibid.*, 5, 179 (1894).

[12] Baxter, Tani and Chapin, THIS JOURNAL, 43, 1080 (1921).

Lanthanum Nitrate.—The apparent molecular weight of the hydrated salt was determined by igniting a weighed sample to lanthanum oxide.

Lanthanum Chloride.—The apparent molecular weight of this hydrate was determined by analyzing for chloride by the Mohr method. All salts were kept in glass-stoppered bottles sealed with paraffin.

Water.—Distilled water was redistilled over potassium permanganate acidified with phosphoric acid, through a block tin condenser, with steam escaping. The combined ammonia and indicator "blank" on water prepared in this manner amounted to 0.04–0.05 cc. of 0.02073 N HCl for a 100-cc. aliquot. The water was stored in pyrex "resistance glass" bottles, but never for a period longer than a week or ten days.

5. The Data at High Dilution

The solubility relations of two tri-univalent cobaltammines in very high dilutions of aqueous potassium sulfate at 25° are given herewith.

Table I

Luteo-cobaltic Di-ammino Tetra-nitro Cobaltiate, LN_3

HCl = 0.01031 N. Sample aliquot, 100 cc. Water blank, 0.06 cc.

Solvent	No. of detns.	Av. cc. of HCl, corr.	Av. dev.	Soly. in moles per liter × 10^4	μ	$\sqrt{\mu}$	Log S/S_0
Water	8	19.10	0.03	1.641	0.0009852	0.03139	...
K_2SO_4							
0.0002 *M*	3	20.80	.01	1.787	.001672	.04089	0.0371
.0005 *M*	3	23.18	.02	1.991	.002695	.05191	.0841
.0010 *M*	5	26.05	.03	2.238	.004343	.06590	.1348

Table II

Luteo-cobaltic Di-ammino Di-nitro Oxalo Cobaltiate, LON_3

HCl = 0.01031 N. Sample aliquot, 200 cc. Water blank, 0.11 cc.

Solvent	No. of detns.	Av. cc. of HCl corr.	Av. dev.	Soly. in moles per liter × 10^4	μ	$\sqrt{\mu}$	Log S/S_0
Water	8	19.22	0.03	0.8255	0.0004953	0.02226	...
K_2SO_4							
0.0002 *M*	3	21.50	.01	0.90236	.001154	.03397	0.0487
.0005 *M*	3	24.13	.01	1.036	.002122	.04607	.0989

The column "Av. cc. of HCl" gives the average amount of acid used to neutralize the ammonia distilled for the number of determinations indicated in the second column. "Av. dev." represents the average deviations of the individual determinations from this average. The fifth column gives the solubility of the saturating salt in moles per liter at 25 ± 0.007°. μ is the ionic strength. The last column gives the values for the relation log S/S_0, where "S" is the solubility of the saturating salt in the neutral salt solution and "S_0" the solubility in pure water.

6. Discussion of Results

The values obtained for the solubility of the present preparations of the two luteo-cobaltic salts in pure water agree with those found by La Mer and Mason for the LN_3 salt within 0.6%, and for the LOn_3 salt within 0.2%.

Similarly, their results, in which they found marked deviations from the theory given by Debye and Hückel for the case where these two cobalt-ammine salts were dissolved in potassium sulfate solutions, have been confirmed. The deviations have been found to persist down to even more dilute solutions, namely, to a solution of 0.0002 M K_2SO_4. In the figure the values of log S/S_0 are plotted against the square root of the ionic strength. I represents the curve for the LN_3 salt, II the curve for the LOn_3 salt, while the dotted lines represent the curves demanded by the limiting law for the respective salts. The experimental curves give no evidence whatever of fusing into the theoretical at the highest dilutions possible with this salt. The initial slopes of these experimental curves for

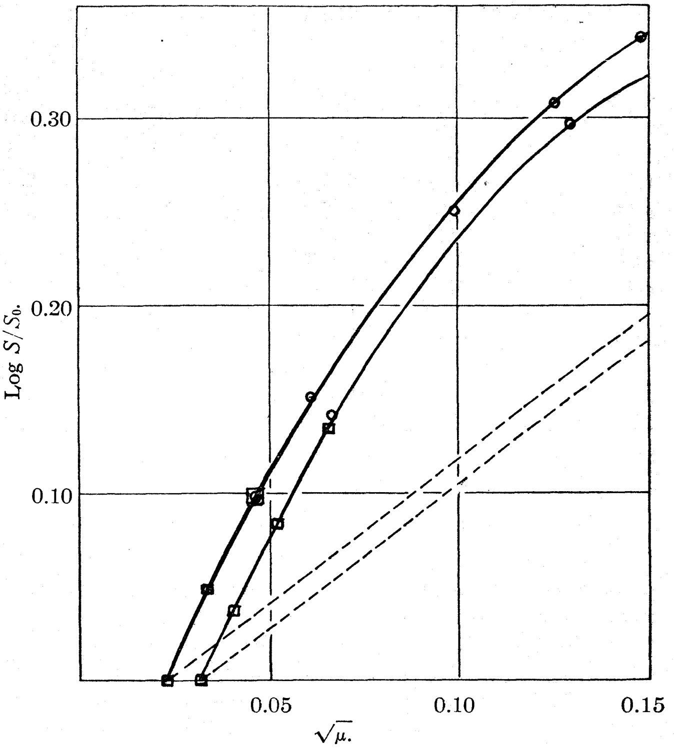

Fig. 1.—The solubility effects of potassium sulfate on luteo-cobaltic diammino tetranitro cobaltiate, I, and luteo-cobaltic diammino dinitro oxalo cobaltiate, II, at high dilution. The upper curve is II, the lower I. The dotted lines represent the slopes of the Debye–Hückel limiting law for each salt. ⊡, This investigation; ⊙, La Mer and Mason.

the highly dilute regions (μ = 0.0005 – 0.002, and 0.001 – 0.0027) give "apparent" values for the constant α' of 1.4, which is nearly three times the theoretical value at 25°, namely, 0.504.[5,7]

7. The Data at 0.1 N Concentration

TABLE III

LUTEO-COBALTIC DI-AMMINO DI-NITRO OXALO COBALTIATE — $Co(NH_3)_6[Co(NH_3)_2(NO_2)_2C_2O_4]_3$

LUTEO-COBALTIC COBALTICYANIDE[a] — $Co(NH_3)_6Co(CN)_6$

Solvent salt solns., all 0.1 N	No. of detns.	Molar soly. $\times 10^4$	No. of detns.	Molar soly. $\times 10^4$
KNO_3	12	2.030	3	1.978
KCl	4	2.006	2	2.018
K_2SO_4	5	3.438	5	5.920
$NaNO_3$	4	1.954	3	1.864
NaCl	3	1.935	6	1.857
Na_2SO_4	4	3.348	3	5.623
$Mg(NO_3)_2$	3	1.928	3	2.415
$MgCl_2$	3	1.905	3	2.381
$MgSO_4$	3	2.818	3	4.619
$La(NO_3)_3$	3	2.615	3	3.301
$LaCl_3$	3	2.590	2	3.384

[a] For measurements on this salt at high dilution see Bronsted and Brumbaugh, THIS JOURNAL, **48**, 2015 (1926).

TABLE IV

LUTEO-COBALTIC DI-AMMINO TETRA-NITRO COBALTIATE

$Co(NH_3)_6[Co(NH_3)_2(NO_2)_4]_3$

Solvent salt solns., all 0.1 N	No. of detns.	Molar soly $\times 10^4$
KNO_3	3	3.790
KCl	5	3.753
K_2SO_4	4	6.432

TABLE V

LUTEO-COBALTIC FERRICYANIDE

$Co(NH_3)_6Fe(CN)_6$

Solvent salt solns., all 0.1 N	No. of detns.	Molar soly. $\times 10^4$
KNO_3	6	2.739
KCl	6	2.789
$NaNO_3$	4	2.572
NaCl	2	2.577

For measurements on this salt at high dilution see ref. 7.

TABLE VI

SOLUBILITY RATIOS AT 0.1 N CONCENTRATIONS

Saturating salts Type	Salt	Cation present		NO_3/Cl	Ideal value		SO_4/Cl		SO_4/NO_3	Ideal value
(3, −1)	LON_3	K		1.012			1.714		1.694	1.281
		Na		1.010			1.730		1.714	
		Mg	(a)	1.012	1.000	(f)	1.479	(j)	1.461	1.229
		La		1.010			(1)		(1)	
(3, −1)	LN_3	K		1.010			1.713		1.697	1 281
			Av. =	1.011						

Table VI (*Concluded*)

Saturating salts Type	Salt	Cation present		NO_3/Cl	Ideal value		SO_4/Cl		SO_4/NO_3	Ideal value
(3, −3)	LC	K	(b)	0.980	1.000	(g)	2.934	(k)	2.993	2.102
		Na		1.004			3.028		3.017	
		Mg		1.014			1.940		1.913	1.854
		La		0.976			(*a*)		(*a*)	
(3, −3)	LF	K		0.982			(*b*)		(*b*)	
		Na		0.998			(*b*)		(*b*)	
			Av. =	0.992						

Table VII

Solubility Ratios at 0.1 *N* Concentrations

Saturating salts Type Salt	Anion present		K/Na	Ideal value		K/Mg	Ideal value		K/La	Ideal value
$(3, -1)LOn_3$	NO_3	(c)	1.039	1.000	(h)	1.053	0.780	(l)	0.776	0.634
	Cl		1.037			1.053			0.775	
	SO_4		1.027			1.220	0.814		(1)	
(3, −3)LC	NO_3	(d)	1.061	1.000	(i)	0.819			0.599	0.255
	Cl		1.087			0.848			0.596	
	SO_4		1.053			1.282	0.539		(*a*)	
(3, −3)LF	NO_3	(e)	1.065	1.000		(*b*)			(*b*)	
	Cl		1.082			(*b*)			(*b*)	

[a] Not determined, see Section 8. [b] Not determined.

8. Discussion of Results

Tables III, IV and V give the respective solubilities in 0.1 N solutions of the solvents indicated. It was impossible to include lanthanum sulfate as one of the solvent salts since crystals of some less soluble salt, possibly a double salt, separated out. Table VI summarizes the anion solubility ratios for the four saturating salts; also the ideal values for the ratios as predicted by the Debye-Hückel limiting law. Table VII gives the cation ratios in the presence of the common anions.

According to Equations 1 and 2, the bracketed groups labeled (a), (b), (c), etc., designate groups within which the ratios should be identical if the principle of specific interaction holds for all valence types of solvents at the same equivalent concentration. The numerical values in group (a) are not necessarily equal to those in group (b) since they represent ratios for two different valence types of saturating salts. Groups (c), (d) and (e) of Table VII should be constant within each group but not necessarily to each other, since here the anions of the saturating salts are different (Equation 2a).

If the principle of ionic strength were true at 0.1 N concentrations, all of the values in groups (a), (b), (c), (d) and (e) should be equal to unity, which is obviously not the case; the deviations from this principle vary from 2.7 to 8.7% for groups (c), (d) and (e), while the corresponding variations from the principle of specific interaction are 0.2% for NO_3^- to Cl^- in group (c) to 3.4% between Cl and SO_4 in group (d). Table III contains the most striking departure from the ionic strength principle which we have ever noted. The solubilities of the (3, – 3) LC salt change from 2.381 to $5.920 \cdot 10^{-4}$ mole liter in passing from 0.1 *N* $MgCl_2$ to 0.1 *N* K_2SO_4. The ionic strengths of the solvents are identical yet the ratio of the solubilities is 2.55 instead of 1.00.

In considering groups (f), (g), (j), (h), (k) and (i), where the ratios involve ions of different valence, it will be observed that the values remain constant only when the ideal values as given by the Debye limiting law also remain constant. In other words, *it is only when the ratios of the ionic strengths of the solvents remain constant, as well as the equivalent concentrations, that the numerical comparisons of principle of specific interaction can be applied.*

The solubility ratios for SO_4/Cl or SO_4/NO_3 change by 25% for LOn₃ and by 35% for LC, when the common univalent cation (K or Na) is exchanged for the bivalent cation Mg. A similar result holds for the cation ratios K/Mg in Table VII when the common anion changes from NO_3 or Cl to SO_4.

According to the Debye-Hückel theory, one might expect that this difficulty could be avoided by making all comparisons at the same ionic strength but, as can be pointed out more clearly in the next paper with $TlIO_3$, this procedure does not seem to work in agreement with the earlier statement of Brönsted.[13]

Nor does the equally plausible scheme of comparing *only the activity deviations* at the same equivalent concentrations, instead of the total activity coefficient, assist very materially. The reader may readily verify this statement by dividing the observed ratios in Tables VI and VII by the corresponding ideal values to eliminate the change in primary Milner effect. The change in the ideal values with valence type is too small to bring about the desired constancy.

Accepting the restriction that the valence types of the solvents must be chosen such that the comparisons do not involve a change in the ideal value, our data furnish some excellent confirmations of the principle of specific interaction. Thus the NO_3/Cl, SO_4/Cl and SO_4/NO_3 ratios are identical for the LN_3 and LOn_3 salts within 0.2% in the presence of K ion, as they should be, since the saturating salts contain the same cation (verification of Equations 1 and 2). This confirmation is particularly significant in view of the fact that not only are the ratios quite different from the ideal values for 0.1 *N* levels, but the Debye limiting law breaks down completely for both of these salts at such small additions as 0.0002 M K_2SO_4 (Parts 5 and 6).

Although the values in group (b) show slight variations when the common cation changes from K to Mg and finally to La, it should be noted that

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[13] Ref. 2 a, p. 2909; *see* ref. 6.

changing the anion of the saturating salt from C^{---} to F^{---} produces a variation of only 0.2% in the presence of K and of 0.6% in the presence of Na. The constancy of the K/La and K/Mg ratios when the common anion is changed from NO_3 to Cl also deserves mention in extending the limits of applicability to higher valence types of solvents.

Since the saturating salts involve two different valence types, we can calculate the ratios of the interaction coefficients r_i of chlorides and nitrates, and of sulfates and chlorides, on the luteo cobaltic ion from the values given in Table VI by the methods outlined in detail by Brönsted,[14] and also, the ratios of the salting out coefficients (r_u).

The products of r_u by r_i give r_f, the ratios of the activity coefficients. These calculations yield

TABLE VIII[a]

CHLORIDE/NITRATE RATIOS

In presence of cation	r_i	r_u	r_f
K^+	0.883	1.043	0.921
Na^+	0.976	1.016	0.992
Mg^{++}	1.008	1.010	1.018
La^{+++}	0.872	1.045	0.911

CHLORIDE/SULFATE RATIOS

In presence of cation	r_i	r_u	r_f
K^+	8.60	1.001	8.60
Na^+	9.39	0.988	9.28

[a] The ratios of the interaction coefficients do not appear to be entirely independent of the other ions in the solution, as demanded by the principle. The nature of the calculation, however, makes the values extremely sensitive to small errors in the measurements, so that the disagreements may not be as marked as appears at first sight. Using (1, −1) and (1, −2) as saturating salts, Bronsted found the salting out ratio $r_u(Cl/SO_4)$ to be about 1.01, while our ratios based on (3, −1) and (3, −3) saturating salts are 1.00 and 0.99 in the presence of K and Na, respectively.

Summary and Conclusions

The principle of specific interaction has been given an extensive experimental test by means of solubility measurements on high valence types of mixtures, using (3,−1) and (3,−3) saturating salts in the presence of (1,−1), (1,−2) (2,−1), (2,−2) and (3,−1) types of solvent salts at 0.1 N concentrations. It is shown that the principle can be extended to higher valence solvents provided that comparisons are restricted to types in which the ratio of the ionic strengths remains unchanged when changing the common solvent ion at the same equivalent concentration.

The results of La Mer and Mason, in which they found very marked deviations from the limiting law of Debye and Hückel at high dilutions when the ions of opposite sign are of high valence, have been confirmed.

The principle of specific interaction retains its validity in these cases in

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[14] Ref. 2 a, pp. 885 ff.

spite of the failure of the Debye limiting law to hold at concentrations as low as 0.0005μ.

NEW YORK, N. Y.

[CONTRIBUTION No. 607 PROM THE DEPARTMENT OR CHEMISTRY, COLUMBIA UNIVERSITY]

ACTIVITY COEFFICIENTS OF ELECTROLYTES. IV. THE SOLUBILITIES OF LANTHANUM AND THALLOUS IODATES IN AQUEOUS SALT SOLUTIONS AND THE PRINCIPLE OF SPECIFIC INTERACTION[1]

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1. Introduction

The purpose of this investigation was to determine (a) whether or not the highly abnormal results (from the viewpoint of the present form of the Debye-Hiickel Theory) obtained in this Laboratory by La Mer and Mason,[2] and since confirmed by Dr. Graham Cook,[3] for the solubilities of tri-univalent cobaltammines dissolved in solvents containing high valence anions were general phenomena, or simply specialized cases peculiar to the cobaltammine family; and (b) in how far Bronsted's principle of specific interaction would hold for other types of salt mixtures where the principle of ionic strength and the present form of the Debye-Hiickel theory have proved to be inadequate.

To answer these questions the solubility of lanthanum iodate was measured, using aqueous solutions of the chlorides, nitrates and sulfates of potassium, sodium, magnesium, lanthanum and zinc as solvents. Lanthanum iodate is particularly suited for this study since La^{+++} is the only trivalent cation, aside from the cobaltammine ions like $[Co(NH_3)_6]^{+++}$, which does not appreciably hydrolyze in aqueous solution. The neutrality of the lanthanum solutions was proved by colorimetric tests and by the fact that iodine was not liberated on addition of potassium iodide until free acid was added.

Similar studies were made of the solubility of thallous iodate in order to have a symmetrical uni-univalent salt with the same anion for comparison with lanthanum iodate.

These saturating salts are stable[4] and of an appropriate order of solubil-

[1] Preliminary reports of this work were presented at the Detroit (September, 1927) and Swampscott (September, 1928) meetings of the American Chemical Society. The present paper is constructed from a Dissertation by F. H. Goldman submitted to The Faculty of Pure Science, Columbia University, in October, 1928, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] La Mer and Mason, THIS JOURNAL, 49, 410 (1927).

[3] La Mer and Cook, *ibid.*, 51, 2622 (1929).

[4] Sadolin, *Z. anorg. allgem. Chem.*, 160, 133 (1927); see ref 5 c.

ity, the solubility of lanthanum iodate being 0.0008901 molar at 25°, while thallous iodate is 0.001844 molar. The latter is nine times as insoluble as thallous chloride, which has been much used by previous investigators.[5] The iodate can also be analyzed more accurately and more easily than the chloride. Thus one mole of thallous iodate reacting with potassium iodide furnishes six equivalents of iodine; while one mole of lanthanum iodate furnishes eighteen equivalents! Furthermore, it is possible to use solutions of salts with an ion in common as solvents, *e.* g., lanthanum sulfate, lanthanum chloride, lanthanum nitrate, without causing the solubility to decrease below the point of analytical detection.

The only previous[6] solubility measurements on lanthanum iodate were made by Harkins and Pearce.[7] They measured the solubility of this salt in the presence of lanthanum nitrate, lanthanum ammonium nitrate and sodium nitrate. In utilizing these measurements to test the validity of the principle of ionic strength, Lewis and Randall[8] say, "Unfortunately an error seems to have slipped into the first two of these series" (lanthanum nitrate and lanthanum ammonium nitrate). This criticism adds particular interest to the study of this salt, since in the light of La Mer and Mason's investigations it is reasonable to suppose that the difficulty might be due to the failure of the principle of ionic strength and not to the data.

2. Theoretical

Debye and Hückel,[9] on the basis of the first approximation of the solution of the Poisson-Boltzmann equation, attempt to take "ion size" into account to explain the individual deviations from the limiting law which appear in the less highly dilute solutions. They get the following expression[10] for the activity coefficient of the solute

$$-\log_{10} f = \frac{\alpha' \, (-Z_1Z_2) \, \sqrt{\mu}}{1 + \text{“}a\text{”} \, \kappa} \tag{1}$$

where "*a*" is the distance of closest approach of the ions in Å. (10^{-8} cm.) units and $\kappa = 0.327 \times 10^8 \sqrt{\mu}$. This expression seems to hold very well for the lower valence types of salts up to concentrations of about 0.2μ, but is inadequate in the case of aqueous solutions where high valence ions of opposite sign are involved, as well as for most non-aqueous solutions.

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[5] (a) Bray and Winninghoff, THIS JOURNAL, *33, 1663 (1911);* (b) *Butler* and Hiscocks, *J. Chem. Soc.,* 2554 *(1926)*; (c) Randall and Chang, THIS JOURNAL, *50,1535 (1928).*

[6] Aside from the conductimetric measurements of Rimbach and Schubert, quoted in "International Critical Tables," Vol. IV, p. *227,* where $S_0 = 0.00254$. This value is in error by *250%.*

[7] Harkins and Pearce, THIS JOURNAL, *38,2679 (1916).*

[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, *1923,* p. *378.*

[9] Debye and Hückel, *Physik. Z.,* 24, *185, 343 (1923).*

[10] See ref. 2, p. *417, Eq. 2.* This equation contains a misprint. The fraction should read $1/(1 + x)$ not $x/(1 + x)$.

For extremely dilute solutions (κ small), the denominator approaches unity, and Equation 1 reduces to the limiting law, which is independent of specific properties of the ions. In a saturated solution the activity coefficient of the solute is determined by the following relationship[11]

$$\log S/S_0 = \log f_0/f \qquad (2)$$

S is the solubility of the saturating salt in the salt solution under consideration; S_0 is the solubility of the saturating salt in pure water; f_0 is the activity coefficient of the saturating salt in water, which may arbitrarily be set equal to unity for a very slightly soluble salt, but can be determined by extrapolating the curve obtained in high dilution to infinite dilution.

The activity coefficient determined from Equation 2 is an observed value; that determined from Equation 1, a calculated value. From Equation 1 it can be seen that all deviations between the observed and calculated values of $\log f$, if negative, could be accounted for by assuming a larger value for "a." On the other hand, positive deviations could only be accounted for in this equation by assuming negative values of "a," which are physically absurd.

Gronwall, La Mer and Sandved[12] have recently obtained a complete solution of the Poisson-Boltzmann equation, whereby additional terms involving *only* the parameter "a" are introduced into Equation 1. This obviates the difficulty of negative values of "a," and they are thus able to account entirely for the discrepancies between theory and experiment *for salts of symmetrical valence types* up to values of $x = a\kappa$ equal to about 0.3, using values of "a" which are physically reasonable. The calculations for the unsymmetrical types studied by La Mer and Mason[2] are too complex for a complete theoretical treatment along these lines, but it appears likely that when the necessary numerical computations are available for these types, this purely mathematical extension will also account for most of these deviations.

In the meantime it is desirable to see how far the experimental results can be correlated with less complicated semi-empirical treatments, of which Brönsted's principle of specific interaction appears to be the most promising. For the development of this theory the reader must consult the original papers[13] and the preceding article."

3. Preparation of Materials

Lanthanum Iodate.—Sixty grams of cerium-free lanthanum nitrate in solution and 130 g. of potassium iodate in solution were added dropwise and simultaneously to approximately fifteen liters of distilled water, the addition taking four to five hours. The mixture was thoroughly agitated by an electric stirrer and the stirring continued for three or four days. The precipitate was washed by decantation four times and then allowed to digest for two weeks in about two liters of water at 70° with stirring. The salt

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[11] Bronsted and La Mer, THIS JOURNAL, 46,555 (1924).

[12] Gronwall, La Mer and Sandved, *Physik. Z.*, 29,358 (1928).

[13] (a) Bronsted, THIS JOURNAL, 44, 877 (1922); (b) 45, 2898 (1923); (c) *Trans. Faraday Soc.*, 23,416 (1927).

so obtained was "sedimented"[2] in a tall narrow cylinder (2 X 100 cm.) several times and the finer material remaining at the top each time was rejected.

Thallous Iodate.--Eighty grams of potassium iodate in solution and 100 g. of thallous nitrate were added dropwise and simultaneously to six liters of water at 60° with constant stirring. The precipitate was allowed to digest and the stirring continuecl. The salt was washed by decantation six times with water, after which it was placed in a beaker containing 500 cc. of water and allowed to digest on a hot-plate at 80°. It was then "sedimented" to obtain crystals of uniform size.

The same preparations of potassium, sodium, magnesium and lanthanum salts whose purification has been described in detail in the preceding paper (La Mer and Cook) were used in this work. In addition lanthanum sulfate, especially freed from cerium for us by the Welsbach Company, was used. Its "apparent" molecular weight was determined by precipitating a sample as oxalate, igniting, moistening with nitric acid and reigniting to the oxide. Kahlbaum's "Zur Analyse" zinc sulfate was dried to constant weight in an air-bath and kept in a desiccator over sulfuric acid.

The solubility measurements were performed with the same apparatus and with the same necessary precautions that have been described in detail in the first paper of this series.

Lanthanum iodate was determined by dissolving three grams of potassium iodide in 10 cc. of boiled water in a 500-cc. iodine flask, adding a 25-cc. aliquot of solution from a volumetric flask, then three rinsings with distilled water and finally 2 cc. of 9 M sulfuric acid. After standing for five minutes in the dark, the contents were then titrated with sodium thiosulfate from a weight buret, using starch as indicator. Duplicate determinations checked to one part in two thousand. The average deviation of eleven determinations of the solubility of lanthanum iodate in water extending over a period of five months was only nine parts in ten thousand. Equilibrium was checked by allowing a solution saturated at 35° to flow through a column of lanthanum iodate at 25°. No change in solubility was found when the saturated solution was allowed to run through the column a second time. Blanks on the potassium iodide were negative.

The thiosulfate solutions were restandardized each week against potassium permanganate and could be checked to 0.1%.[14]

When the same analytical method was tried for thallous iodate a difficulty was encountered. An insoluble yellow precipitate was obtained when sodium thiosulfate was added in the course of the titration. In the presence of thallous ion thiosulfate is reduced to thallous sulfide.[15]

The following modification was found satisfactory. Sodium arsenite was used instead of sodium thiosulfate; only one cc. of nine molar sulfuric acid was added. The flask was then placed in the dark for five minutes, fifty cc. of a solution containing 3 g. of sodium bicarbonate was added and the contents of the flask titrated with standard sodium arsenite, using starch as an indicator. The end-point was obtained by back titrating with standard iodine solution. Determinations differed from one another by not more than four parts in a thousand.

The sodium arsenite solution used was 0.0150 N and was prepared as a primary standard according to directions in Scott,[16] using Kahlbaum's "Zur Analyse" arsenious oxide, and checked against potassium permanganate.[17] The two methods agreed to one part in a thousand.

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[14] Eray and Miller, THIS JOURNAL, 46,2204 (1924).

[15] Mellor, "Inorganic and Theoretical Chemistry," Longmans, Vol. V, p. 424.

[16] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, New York, 1920, Vol. I, p. 240.

[17] Diess, *Chem.-Ztg.*, 38, 413 (1914).

4. Discussion of Data

Table I gives the solubility of lanthanum iodate in aqueous solutions of potassium chloride, potassium sulfate and lanthanum nitrate. The concentrations of the solvent salts are given in Col. 2. Column 4 gives the value of the logarithm of the ratio of the solubility in the particular solvent, to the solubility in pure water, S_0. When the values $z_1 = 3$, $z_2 = -1$ and $\alpha' = 0.505$ are introduced, Equation 1 takes the limiting form

$$-\log f = 1.515\sqrt{\mu} \qquad (3)$$

at 25° using 78.77 for D, the dielectric constant of water.

TABLE I

SOLUBILITY OR $La(IO_3)_3$

Sample No. 1

No. of detns.	Moles/ liter of added salt	Soly. in moles/ liter	Log S/S_0	$-\text{Log } f$	μ	$\sqrt{\mu}$	$-\text{Log } f$ (calcd.)	Log f (obs.) —log f (calcd.)
				H_2O				
11	....	0.00089006	...	...	0.005340	0.07308	0.1107	......
				K_2SO_4				
6	0.0002	.00091666	0.01279	0.12349	.006100	.07810	.1183	+0.0052
4	.0005	.00097463	.03934	.1500	.007347	.08571	.1299	.0201
4	.001	.0010564	.07429	.1850	.009337	.09663	.1464	.0386
4	.002	.0012153	.13536	.2461	.013293	.1153	.1747	.0714
4	.007	.0016852	.27718	.3879	.031110	.1764	.2672	.1207
4	.0125	.0020272	.35748	.4682	.04966	.2228	.3376	.1306
4	.02	.0023675	.42482	.5355	.07420	.2724	.4127	.1228
4	.05	.0031871	.55078^{a}	.6615	.16912	.4112	.6230	.0385
				KCl				
2	.001	.00091128	.01015	.1203	.006467	.08042	.1218	− .0010
5	.005	.00097490	.03959	.1503	.01085	.1042	.1578	− .0075
4	.01	.0010322	.06436	.1751	.01619	.1272	.1928	− .0177
4	.05	.0013331	.17552	.2862	.05800	.2408	.3649	− .0787
2	.1	.0015713	.24250^{b}	.3532	.1094	.3308	.5011	− .1479
2	.2	.0018776	.32423	.4349	.21127	.4597	.6964	− .2615
2	.5	.0025641	.45465^{c}	.5653	.51538	.7179	1.088	− .523
4	1.0027	.0030547	.53068^{c}	.6414	1.021	1.010	1.531	− .890
4	2.000	.0037828	.62356^{c}	.7343	2.023	1.422	2.155	−1.421
				$\text{Log}\sqrt[4]{\frac{Ksp}{K_0sp}}$ $La(NO_3)_3$				
				Sample No. 3				
7	none	.0009482	...	...	.005689	.07543	.1143	......
2	.001667	.0008347	.0638	.1781	.01501	.1225	.1856	− .0075
3	.003333	.0008101	.1088	.2231	.02486	.1577	.2389	− .0158
4	.01667	.0008696	.2886	.4029	.1052	.3243	.4914	− .0885
3	.03333	.0009398^{d}	,3781	.4920	.2056	.4534	.6869	− .1949

[a] $S_0 = 0.0008967$. [b] $S_0 = 0.0008989$. [c] $S_0 = 0.0009000$. [d] $S_0 = 0.0009426$.

TABLE II

SOLUBILITY OF $La(IO_3)_3$ AT 25° IN VARIOUS 0.1 *N* SOLVENTS

Sample No. 2

Solvent	No. of detns.	Solubility, mole/liter	Solvent	No. of detns.	Solubility, mole/liter
S_0	5	0.0009426	$M/10$ KNO_3	4	0.001679
$M/30$ $La_2(SO_4)_3$	2	.001830	$M/10$ $NaNO_3$	3	.001654
$M/60$ $La_2(SO_4)_3$	2	.001532	$5M/100$ K_2SO_4	4	.003370
$M/30$ $La(NO_3)_3$	3	.0009398	$5M/100$ Na_2SO_4	4	.003326
$M/30$ $LaCl_3$	4	.0009233	$5M/100$ $MgSO_4$	2	.002997
$M/10$ NaCl	2	.001627	$5M/100$ $Mg(NO_3)_2$	4	.001766
$M/10$ KCl	2	.001648	$5M/100$ $MgCl_2$	4	.001739

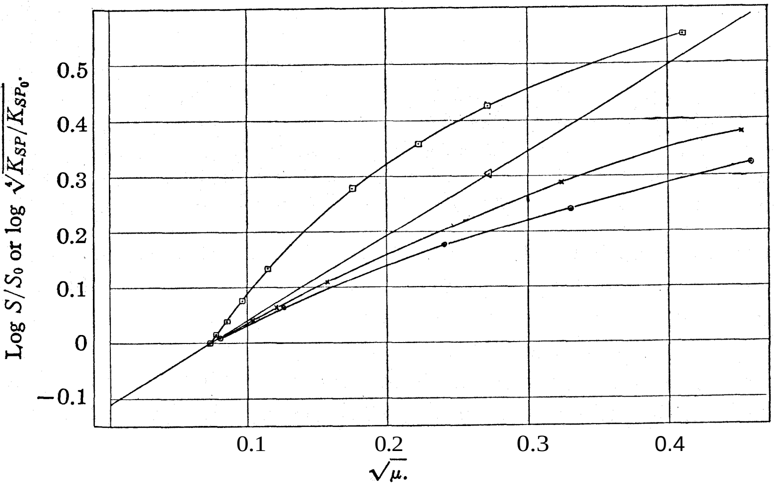
From this equation $-\log f_0 = 0.1107$. By introducing this value into Equation 2 we get the values for $-\log f$ given in Col. 5. Column 8 gives $-\log f$ calculated from Equation 3, and Col. 9 gives the difference between this value and the observed value.

It should be noted that of the three solvents in this table, potassium sulfate has the greatest effect on the solubility of lanthanum iodate. The solubility of lanthanum iodate is three and one-half times as great in a 0.1 N solution of potassium sulfate as in pure water. In addition potassium sulfate exhibits marked positive deviations from the limiting law.

In the case of lanthanum nitrate, which has an ion in common with lanthanum iodate, it is necessary to consider the ratio of the stoichiometric solubility product constants[n] rather than the solubilities. Therefore in the case of lanthanum nitrate, Col. 3 represents log $\sqrt[4]{Ksp/K_0sp}$. It is interesting to note that in changing the concentration of lanthanum nitrate from 0.003333 M to 0.01667 M the solubility of lanthanum iodate instead of decreasing, actually increases almost 6%, showing that in the case of a salt of high valence type the depression in solubility due to the common ion effect is soon obliterated by the more important factor, the change in the activity coefficient of the saturating salt. This is better seen by examining the data for the solubility of this salt in lanthanum sulfate, a (3,–2) solvent salt with an ion in common (see Table 11). At sixtieth molar (0.1 *N*) the solubility is already 55% higher than in pure water!

These data should be of interest to the analytical chemist, especially when planning new procedures. For instance, before washing a precipitate with a salt solution having an ion in common, the point where minimum solubility occurs should be determined, instead of relying entirely on a stoichiometrical calculation of the solubility product.

The results in Table I are plotted in Fig. 1. The line marked "limiting tangent" is the limiting law of Debye and Hückel. From the figure it is evident that the curve for potassium sulfate does not fuse into the theoretical slope, but shows a maximum deviation, or "hump;" also that while the potassium chloride and lanthanum nitrate curves do fuse into the theoretical line, the latter deviates less than the former from the limiting law. This behavior is quite parallel to that observed by La Mer and Mason[2] (see their Figs. 2 and 3) using cobaltammines.



▽—Limiting tangent; ⊙—KCl; ⊡—K_2SO_4; ×—$La(NO_3)_3$.

Fig. 1.

The solubility of thallous iodate is given in Table III. The column headings have the same significance here as in Table I.

TABLE III

SOLUBILITY $TlIO_3$

Log f_0 = 0.02169; −log f = 0.505 $\sqrt{\mu}$ at 25°

No. of detns.	Moles/liter of added salt	Soly. in mole/liter	Log S/S_0	−Log f	−Log f calcd.	Log f(obs.) − log f (calcd.)	μ	$\sqrt{\mu}$
H_2O								
15	....	0.001844	...	...	0.02169	......	0.001844	0.04294
K_2SO_4								
4	0.001	.001912	0.0157	0.0374	.0354	0.0020	.004912	.07009
4	.002	.001958	.0260	.0477	.0451	.0026	.007958	.08921
4	.005	.002075	.0513	.0730	.0660	.0070	.01708	.1307
4	.01	.002193	.0753	.0970	.0906	.0064	.03219	.1794
4	.013	.002252	.0868	.1085	.1026	.0059	.04125	.2031
4	.03	.002513	.1344	.1561	.1536	.0025	.09251	.3042
4	.03333	.002544	.1398	.1615	.1617	− .0002	.1025	.3202
6	.05	.002747	.1731	.1948	.1973	− .0025	.1527	.3908
4	.064	.002877	.1932	.2149	.2229	− .0080	.1949	.4415
2	.15	.003520	.2808	.3025	.3401	− .0376	.4535	.6734
4	.25	.004028	.3393	.3610	.4385	− .0775	.7540	.8683
4	.5	.005128	.4442	.4659	.6196	− .1537	1.5051	1.227

TABLE III *(Concluded)*

No. of detns.	Moles/liter of added salt	Soly. in mole/liter	Log S/S_0	$-\text{Log } f$	$-\text{Log } f$ calcd.	Log f(obs.) $-\log f$ (calcd.)	μ	$\sqrt{\mu}$
				KNO_3				
4	.01	.001987	.0324	.0541	.0553	− .0012	0.01199	0.1095
3	.02	.002079	.0521	.0738	.0750	− .0012	.02208	.1486
6	.05	.002270	.0903	.1120	.1155	− .0035	.05227	.2286
4	.1	.002492	.1308	.1525	.1617	− .0092	.1025	.3202
3	.3	.003126	.2292	.2509	.2780	− .0271	.3031	.5505
2	.5	.003673	.2993	.3210	.3584	− .0374	.5037	.7097
2	1.0	.004821	.4174	.4391	.5062	− .0671	1.0048	1.002
				$NaNO_3$				
6	0.1	.002486	.1297	.1514	.1617	− .0103	0.1025	0.3202
				Na_2SO_4				
4	.03333	.002543	.1396	.1613	.1617	− .0004	.1025	.3202
4	.05	.002740	.1720	.1937	.1973	− .0036	.1527	.3908
				$MgSO_4$				
4	.005	.002068	.0498	.0715	.0750	− .0035	.02207	.1486
5	.01	.002172	.0711	.0928	.1037	− .0109	.04217	.2054
5	.025	.002387	.1121	.1338	.1616	− .0278	.1024	.3200
3	.05	.002640	.1558	.1775	.2273	− .0498	.2026	.4501
				KCl				
4	.01	.002005	.0363	.0580	.0553	.0027	.01201	.1487
4	.02	.002107	.0579	.0796	.0751	.0045	.02211	.1487
4	.05	.002335	.1025	.1242	.1155	.0087	.05234	.2288
4	.10	.002625	.1534	.1751	.1618	.0133	.1026	.3203
				$MgCl_2$				
4	.03333	.002544	.1398	.1615	.1617	− .0002	.1025	.3202
4	.05	.002744	.1726	.1943	.1973	− .0030	.1527	.3908
				NaCl				
4	.10	.002620	.1525	.1742	.1618	.0124	.1026	.3203
				$Mg(NO_3)_2$				
4	.03333	.002459	.1250	.1467	.1617	− .0150	.1025	.3202
4	.05	.002621	.1527	.1744	.1973	− .0229	.1526	.3906
				$ZnSO_4$				
5	.05	.002789	.1797	.2014	.2274	− .0260	.2028	.4503

Figure 2, which represented these results graphically, as in Fig. 1, shows the same type of curve in solutions of potassium sulfate but here the "hump" which was so pronounced in the case of lanthanum iodate, although present, is barely discernible. In the case of magnesium sulfate as solvent the deviations from the limiting law are negative and of the usual character.

Potassium chloride behaves differently with thallous iodate than with lanthanum iodate. The curve is a straight line exhibiting only positive deviations. At 0.1 *N* the solubility in potassium chloride solution is almost as great as that in potassium sulfate (see Table III). Sodium sulfate and sodium chloride show the same behavior as the potassium salts.

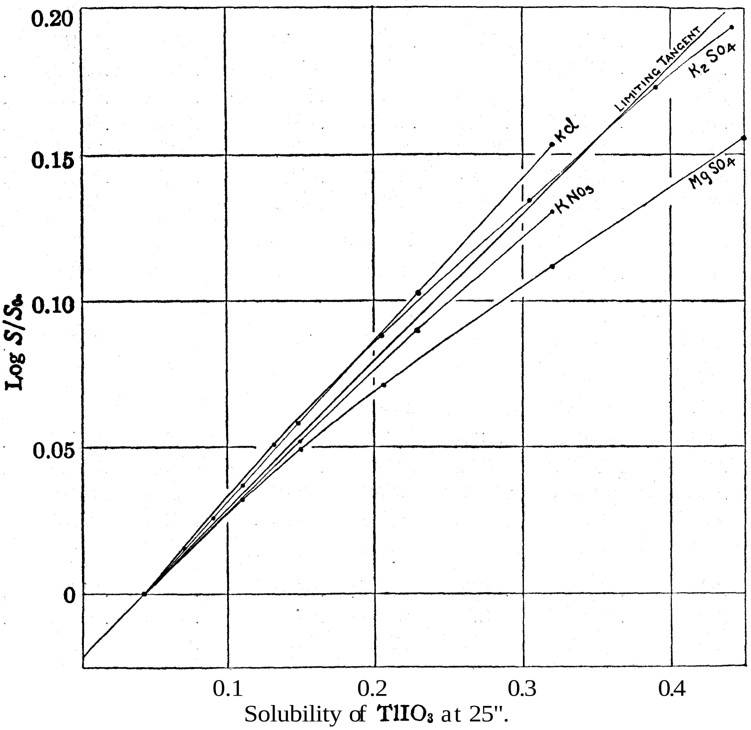


Fig. 2.

Table II contains the solubilities of lanthanum iodate in 0.1 *N* solvents, in order to determine the various solubility ratios for testing the principle of specific interaction.

TABLE IV

SOLUBILITY RELATIONS OF $La(IO_3)_3$ AT 25°

Harkins and Pearce, THIS JOURNAL, 38, 2679 (1916) (Recalculated)

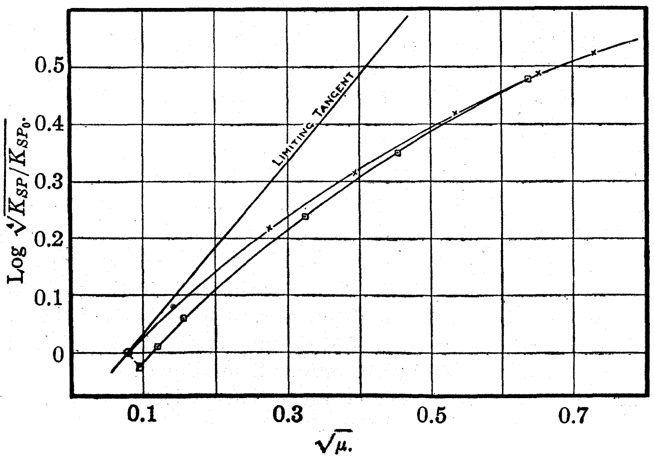
No.	Concn. of added salt, millieq./1000 cc.	Concn. of added salt, mole/1000 cc.	Concn. of sat. salt, millieq./1000 cc.	Concn. of sat. salt, mole/1000 cc.
	Solvent $La(NO_3)_3 \cdot 2NH_4NO_3$, 3 equivalents = 1 mole			
1	26.34	0.008780	2.8530	0.000951
2	56.682	.018894	3.0470	.001057
3	105.364	.035121	3.4102	.0011367
4	158.048	.052683	3.69105	.00123035
5	196.8375	.0656125	3.9184	.00130615
6	393.673	.131224	4.8050	.0016017
7	787.350	.262450	6.1554	.0020518
8	1574.700	.5249	8.6904	.0028968

TABLE IV (*Concluded*)

No.	Concn. of added salt, millieq./1000 cc.	Concn. of added salt, mole/1000 cc.	Concn. of sat. salt, millieq./1000 cc.	Concn. of sat. salt. mole/1000 cc.
		Solvent $La(NO_3)_3$		
9	2.00	.00067	2.5290	.000843
10	5.00	.001667	2.3905	.0007968
11	10.00	.003333	2.3477	.0007826
12	50.00	.01667	2.4960	.0008320
13	100.00	,03333	2.8086	.0009362
14	200.52	.06684	3.3586	.001119

No.	μ	$\sqrt{\mu}$	Log $\sqrt[4]{\frac{K_{sp}}{K_{0sp}}}$	−Log f	−Log f (calcd.)	−Log f (calcd.)
1	0.07595	0.2756	0.2178	0.3378	0.4175	−0.0797
2	.1572	.3965	.3171	.4371	.6007	− .1636
3	.2878	.3365	.4188	.5388	.8127	− .2739
4	.4289	.6549	.4875	.6075	.9922	− .3847
5	.5327	.7299	.5230	.6430	1.106	− .463
6	1.060	1.030	.6714	.7914	1.560	− .769
7	2.111	1.453	.8269	.9469	2.201	−1.254
8	4.227	2.056	1.0142	1.134	3.115	−1.981
9	0.009078	0.09528	−0.0236	0.0964	0.1443	−0.0479
10	.01477	.1215	+ .0110	.1310	.1840	− .0530
11	.02469	.1571	+ .0609	.1809	.2380	− .0571
12	.1049	.3240	+ .2379	.3579	.4909	− .1330
13	.2055	.4535	+ .3495	.4695	.6870	− .2175
14	.4078	.6386	+ .4820	.6020	.9674	− .3654

Table IV contains Harkins and Pearce's[7] data for lanthanum iodate recalculated according to modern theory. Harkins and Pearce state their results only in terms of equivalents, which we interpret in the case of the



×—$La(NO_3)_3 \cdot 2NH_4NO_3$; ⊡—$La(NO_3)_3$.

Fig. 3.

double salt to mean three and not five equivalents per mole. The corresponding curves using lanthanum ammonium nitrate and lanthanum nitrate as solvent salts are given in Fig. 3. Except for the most dilute solutions the agreement with the principle of ionic strength is excellent. Lewis and Randall's failure to confirm their principle in this case evidently rests upon a miscalculation due to the unfortunate ambiguity attached to Harkins and Pearce's meaning of the term equivalent of double salt.

5. Solubility Ratios

Tables V and VI contain the solubility ratios for the saturating salts, $La(IO_3)_3$ and $Tl(IO_3)_3$, in various 0.1 N solvents to test the principle of specific interaction. If the equivalent concentration is the correct scale

TABLE V

$La(IO_3)_3$ SOLUBILITY RATIOS. ALL CONCENTRATIONS ARE AT 0.1 N TO TEST THE THEORY OF SPECIFIC INTERACTION

Cation	NO_3/Cl	Ideal value	SO_4/NO_3	Ideal value	SO_4/Cl	Ideal value
K	1.019	1.000	2.007	1.281	2.045	1.281
Na	1.017		2.011		2.044	
Mg	1.015		1.697	1.232	1.723	1.232
La	1.014		1.449	1.202	1.468	1.202

Anion	K/Na	Ideal value	K/Mg	Na/Mg	Ideal value	K/La	Na/La	Ideal value	Mg/La	Ideal value
NO_3	1.015	1.000	0.951	0.936	0.780	0.727	0.716	0.634	0.765	0.813
Cl	1.013		.948	.935		.723	.714		.763	
SO_4	1.013		1.124	1.110	.812	1.007	.994	.675	.896	.832

TABLE VI

$TlIO_3$ SOLUBILITY RATIOS. CONCENTRATION 0.1 N TO TEST THEORY OF SPECIFIC INTERACTION

Cation	NO_3/Cl	Ideal value	SO_4/NO_3	SO_4/Cl	Ideal value
K	0.949	1.000	1.102	1.046	1.086
Na	949		1.102	1.046	
Mg	.955		1.007	0.962	1.072

Anion	K/Na	Ideal value	K/Mg	Na/Mg	K/Zn	Na/Zn	Ideal value	Zn/Mg	Ideal value
NO_3	1.002	[a] 1.000	0 951	0.949	...	...		...	1.000
Cl	1.002		.957	.955	...	...		...	
SO_4	1.003		1040	1.038	0.985	0.982	0.933	1.056	

[a] Bronsted (ref. 13 a, p. 889) obtains 1.005 for this ratio in the presence of Cl and ClO_3 ions using praseo iodate as the saturating salt. On the basis of Hall and Harkins' values for the freezing point depression of KIO_3 and $NaIO_3$, the principle of specific interaction predicts a value of 1.004 for this ratio. Using Equations 18 and 19 of ref. 13 a we obtain a value of 1.036 for the ratio of interaction for iodate ion; $r_i = r_{IO_3}(Na/K)$ and a value of 0.986 for $r_u = r(Na/K)$ the salting out ratio for Na/K, taking $R_I = 1.004$ and R_{III} (the K/Na solubility ratio for $La(IO_3)_3$) = 1.013 from Table V. The *agreement* between our value for $r(Na/K) = 0.986$ and Brönsted's value (1.011) is not entirely satisfactory.

for these comparisons regardless of the valence type of the solvent, then the ratio within each individual column should be constant. The bracketed values correspond to ratios for which the primary Milner effect is identical, as indicated by the ideal value for the ratio as given by the Debye limiting law. The data substantiate the conclusion of the previous paper that the ratios are constant at 0.1 N only when the ideal value remains unchanged; also that a comparison of the activity deviation coefficients instead of the total activity coefficient at the same equivalent concentration will not yield constant ratios in all *cases since* variation in the ratios which occurs is very much greater than the corresponding change in the ideal value.

On the other hand, limiting the comparisons only to solvent ratio types which should have the same ideal value, we find the principle of specific interaction to be confirmed, as witnessed by the constancy of the bracketed values. In Table V the greatest discrepancy (0.5%) occurs for the NO_3/Cl ratio in passing from the K to the La salts.

The SO_4/NO_3 and SO_4/Cl ratios agree to within 0.2 and 0.05%, respectively, in changing the common cation from K to Na. Since the observed values (2.007 and 2.045) differ markedly from the ideal value (1.281), indicating highly specific effects for the SO_4 ion as opposed to the NO_3 or Cl ion, we must look upon this agreement as an excellent proof that the individual specific interactions are restricted to the ions of opposite sign at least up to 0.1 N. The constancy of the cation ratios of the type K/Mg and Na/La when changing the common anion from NO_3 to Cl is significant for the same reasons, since in previous tests the observed ratios and the ideal ratios have been almost identical, that is to say, the systems chosen have obeyed the Debye limiting law quite closely or have exhibited similar deviations from it.

Table VII gives the solubility ratios for $TlIO_3$ in solvents of various types at the same ionic strength. According to the Lewis and Randall principle of ionic strength,[8] all the ratios should be unity, which is obviously not the case. Although at 0.1 μ the ratios approach their corresponding ideal values somewhat more closely than at 0.1 N, this is partly due to the fact that the higher valence solvents are more dilute in the former case. On the other hand, the constancy of the ratios within a given group is not as good in Table VII as in Table VI. Thus the NO_3/Cl ratio for Mg differs

TABLE VII

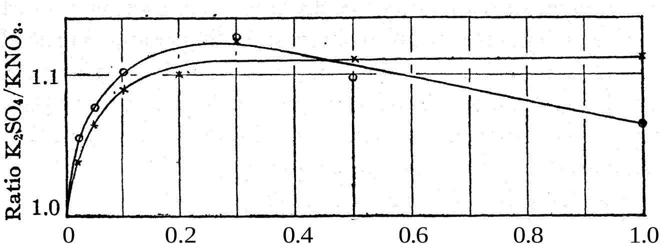
$TlIO_3$ SOLUBILITY RATIOS

Concentration (ionic strength) $\mu = 0.1$ to test principle of ionic strength. Ideal value 1.000 for all.

	NO_3/Cl	SO_4/NO_3	SO_4/Cl		**K/Na**	**K/Mg**	**Na/Mg**
K	0.949	1.021	0.969	NO_3	1.002	1.013	1.011
Na	.949	1.023	.971	Cl	1.002	1.032	1.030
Mg	.967	0.9707	.938	SO_4	1.000	1.066	1.065

by only 0.6% from the identical values for Na and K as cations at 0.1 N, while the corresponding difference amounts to 1.8% at 0.1 μ. Likewise, the K/Mg and Na/Mg ratios in the presence of NO_3 and Cl differ by 0.6% at 0.1 N, whereas the difference becomes 1.9% at 0.1 μ.

Bray and Winninghoff[5a] and Butler and Hiscocks[5b,18] have determined the solubility of thallous chloride in the presence of potassium sulfate and potassium nitrate as solvent salts. From these data the ratio $[S_{TlCl(K_2SO_4)}]/[S_{TlCl(KNO_3)}]$ can be calculated at different concentrations of added salts.



X—TlCl; O—TlIO$_3$.

Fig. 4.

These results appear in Table VIII and are plotted in Fig. 4 together with our data on thallous iodate. Values interpolated from the solubility curves are given in parentheses. Up to 0.3 N the principle of specific interaction is confirmed as well as could be expected when we note that many of the ratios are obtained by combining data from different observers.

Table VIII

Comparison of Specific Interaction Ratios for TlCl and TlIO$_3$

TlCl

Added salt, equiv.	K_2SO_4/KCl	K_2SO_4/KNO_3	KCl/KNO_3
0.02	(1.02) x/o	1.037 x/x	(1.02) o/x
.05	1.073 x/o	1.064 x/x	0.991 o/o
.10	1.066 x/o	1.090 x/x	1.023 o/x
.20	(1.04) x/o	(1.10) x/o	1.063 o/o
.30	(1.04) x/o	1.124 x/x	(1.08) o/x
.50	(0.957) x/o	(1.11) x/o	1.163 o/o
1.0	....	1.127 x/o	....
1.0	....	1.112 x/x	....

x = Bray and Winninghoff; o = Butler and Hiscocks.

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[18] Inadvertently an error crept into the printing of the solubilities of TlCl in $ZnSO_4$. The following corrected values were obtained through communication with Dr. J. A. V. Butler.

Solubility of TlCl in $ZnSO_4$ at 25°

Moles/liter of $ZnSO_4$	0.05	0.1	0.3	0.5994
Solubility	0.02059	0.02279	0.02770	0.03203

TABLE VIII (*Concluded*)

Our data on $TlIO_3$

Added salt, equiv.	K_2SO_4/KCl	K_2SO_4/KNO_3	KCl/KNO_3
0.02	1.041	1.065	1.013
.05	(1.046)	(1.076)	1.029
.10	1.046	1.102	1.053
.30	...	1.126	
.50	...	1.097	
1.0	...	1.064	

Summary and Conclusions

The activity coefficients of lanthanum and thallous iodates have been determined in aqueous solutions of the chlorides, nitrates and sulfates of potassium, sodium, magnesium and lanthanum at 25° by solubility measurements. The usual form of the Debye-Hückel theory does not account for the behavior of a high valence salt like lanthanum iodate in K_2SO_4 solutions. The data show uniformly positive deviations from the Debye-Hückel limiting law and do not fuse into the theoretical curve at least down to concentrations as low as 0.0002 mole of added salt. This behavior is consequently to be looked upon as a general phenomenon and not an isolated one confined to the cobaltammine family. Saturating salts of the (1,–1) type like $TlIO_3$ exhibit positive deviations in sulfate solvents but to a far less marked degree than with $La(IO_3)_3$.

Harkins and Pearce's data for $La(IO_3)_3$ dissolved in $La(NO_3)_3$ as solvent are substantially correct. Lewis and Randall's suggestion that their data for $La(NO_3)_3 \cdot 2NH_4NO_3$ as solvent are in error is not justified and evidently arises from a misinterpretation of the term equivalent of double salt used by Harkins and Pearce.

Bronsted's principle of specific interaction has been tested at 0.1 N concentrations for both saturating salts in various valence types of solvents. Excellent agreement with the requirements of this principle is found whenever the solubility ratios compared at the same equivalent concentration also involve the same ratio of ionic strengths even though the ratios deviate markedly from the ideal value predicted by the Debye limiting law as in the case where sulfates or higher valence cation solvents are involved. The solubility ratios for TlCl and for $TlIO_3$ have been compared for a number of solvents at various concentrations.

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MOLECULAR ORIENTATION AND THE PARTIAL VAPOR PRESSURES OF BINARY MIXTURES.
I. SYSTEMS COMPOSED OF NORMAL LIQUIDS

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Although many measurements have been made of the vapor pressures of solutions containing but one volatile component and the total vapor pressures of great numbers of binary mixtures of volatile liquids have been determined, few experimental data are available on the partial pressures of binary liquid mixtures. Many partial pressures have been calculated from total pressures by means of equations, theoretical and empirical, the success of the calculations depending not only upon the nature of the equations but, unfortunately, upon that of the mixtures as well. An equation recently developed by Langmuir[1] seemed to offer a means not merely of calculating partial pressures but also of learning much about the molecular condition of liquids. In order to examine the applicability of this equation and in order to gain information which might be coordinated with the results of studies of the dielectric polarization of liquids, the measurement of partial vapor pressures was undertaken.

Apparatus and Procedure

The apparatus employed (Fig. 1) was similar in many respects to that used by Sameshima.[2] The vessel A, which had a capacity of 200 cc., contained the liquid mixture, the partial vapor pressures of which were to be measured. A was immersed to the level of the ground-glass stopper S in a carefully regulated thermostat, the temperature of which was approximately 2° above the temperature at which the pressures were to be measured. Superheating was prevented by stirring the liquid electrically by means of a current through platinum spiral B, which was carried by a tube entering the vessel through a ground joint with a mercury seal. The temperature of the boiling liquid was read on the thermometer T, which was suspended by a platinum wire from a hook on the stopper S. The thermometers used were of short range, calibrated in fifths of a degree and standardized at the U. S. Bureau of Standards. The large side tube C was wound with an electric heater, which prevented the condensation of any vapor in C and its subsequent direct return to A. The condensers, D and D′, were surrounded by insulated copper jackets, E and E′, which were filled with solid carbon dioxide in the form of "dry ice." The low temperature obtained with the solid carbon dioxide prevented the escape of vapor and consequent change in the composition of the liquid, which occurred in the preliminary experiments when ice was used for the condensation of the more volatile liquids. In the case of liquids of high freezing point, solidification in the condenser was prevented by inserting a thin sheet of asbestos between the condenser bulbs and the "dry ice." The vapor condensed in D flowed down into the bulb

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[1] Langmuir, "Third Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York, 1925, p. 3.

[2] Sameshima, THIS JOURNAL, 40, 1482 (1918).

F, which had a capacity of about 4 cc. The bulb ordinarily filled within three minutes after the liquid had begun to boil in A and then overflowed through G back into A.

With the aid of the carboys, H and J, which functioned as stabilizers, the pressure was maintained constant during a run by means of the manometer K and a rotary oil pump. When the pressure had been lowered by the pump to a point where the liquid in A boiled at the desired temperature, the platinum wire L, sealed through a small glass tube and attached to a length of copper wire, was adjusted so that its end was at the top of the mercury column, the adjustment being made by sliding the copper wire through the soft wax seal X. This wire and the wire sealed into the manometer at K were connected through a relay, which turned the pump off and on as the mercury column made or broke contact with the wire L at its surface, the pressure thus being kept so constant that no variations could be observed on the manometer N.

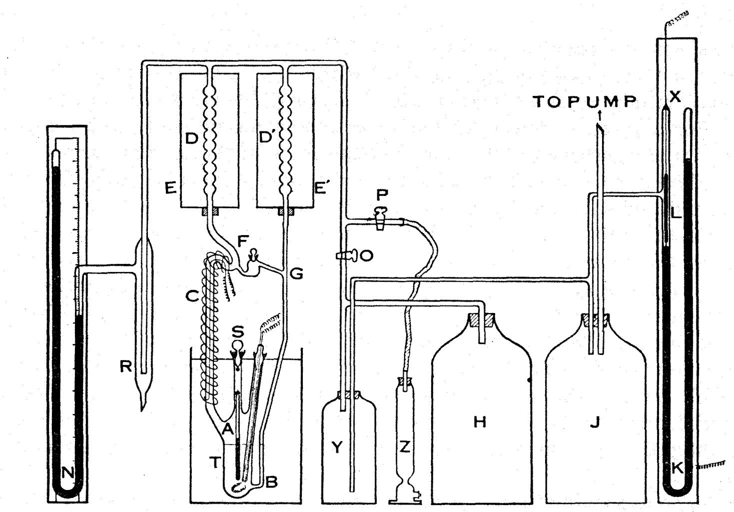

Fig. 1.—Apparatus for vapor pressure measurements.

In order to avoid pressure gradient between A and the manometer N, the tubing used was, for the most part, of 10-mm. internal diameter. The trap R was inserted to keep any liquid which might get into the upper part of the apparatus from running down into the manometer, but this precaution proved unnecessary. The stopcocks O and P were employed to open the main apparatus to atmospheric pressure, while maintaining low pressure in the carboys when desired. Bottles Y and Z contained calcium chloride.

A measurement was carried out in the following manner. About 100 cc. of a mixture, the composition of which was approximately that desired, was placed in Vessel A. The pressure was gradually reduced until, when the electrical stirrer was turned on, the liquid began to boil. The pressure was then regulated until the thermometer constantly indicated the desired temperature. The liquid was allowed to boil for some time, the temperature being kept under careful surveillance. It was found that five or ten minutes were normally sufficient for the attainment of equilibrium conditions, but, for the sake of safety, thirty or forty minutes were usually allowed. The liquid condensed in F now had the composition of the vapor in equilibrium with the liquid in A; 3- or 4-cc. samples were pipetted out of A and F and analyzed by the measurement of their refractive indices as was done by Zawidski.[3] If the mole fractions of the two components of the liquid in F were A and B and the total pressures read on Manometer N were P, the partial pressures of the liquid in Vessel A were AP and BP.

Because of deviations from the ideal gas laws, the partial pressures calculated in this manner are not identical with the pressures which the vapors of the components would exert if allowed to occupy the same volume separately.[4] The results of other investigators have shown that these deviations cause errors of less than 1% in the apparent molecular weights of a large number of vapors measured between 70 and 100°, and Sameshima[2] has found the deviations in mixtures of ether and acetone vapors at 25° to be so small as to be without appreciable effect upon the values of the partial pressures calculated upon the assumption of the applicability of Dalton's law. Even though the deviations may have an appreciable effect in some of the mixtures here studied, the effect should be too slight to impair the use of the results in the examination of Langmuir's theory.

The indices of refraction for the sodium D line were measured with a Pulfrich refractometer, a temperature of 20°, constant within 0.01°, being obtained by a flow of water from carefully adjusted thermostats. The probable error of a measurement was 0.00007. For a given system from twelve to fifteen mixtures of known composition were made up and measured. The molar composition of the mixture corresponding to the observed refractive index if the refractive index were a linear function of composition was calculated and subtracted from the known composition. The differences between the theoretical and the known mole fractions obtained in this way were plotted against the theoretical mole fractions to give a curve which was used to correct the theoretical composition of an unknown mixture of the two liquids calculated from the refractive index on the assumption that the latter was a linear function of the composition. The accuracy of this method of analysis depended upon the precision of the index measurements and upon the difference between the indices of the two components of the mixture. The probable error in the mole fraction was usually 0.001-0.003. The probable error of the partial pressure data was somewhat dependent upon the nature of the liquids under investigation and upon the temperature of the measurement, but was normally 2 ± 1 mm.

In order to ascertain whether or not the apparatus functioned properly, the system benzene–carbon tetrachloride was investigated, the partial pressures being found to duplicate the measurements of Zawidski within the experimental error.[3] The vapor pressure–temperature curves obtained for a number of the pure substances under investigation were found to agree well with the data in the literature.

Purification of Materials

The purification of the materials used is described below. Under each material are given the values of physical constants which serve as criteria of purity. In addition to the boiling point and the refractive index for the sodium D line at 20°, the melting point and the density were occasionally measured. The vapor pressures measured at several temperatures agree well with those given in Landolt-Bornstein, "Tabellen," 5th ed., Berlin, 1923, as previously remarked.

***n*-Hexane.**—A synthetic product obtained from the Eastman Kodak Company was washed repeatedly with slightly diluted sulfuric acid, then with alkaline permanganate solution, dried over sodium, and distilled; b. p. 68.8°; $d_4^{20} = 0.6600$; $n_D^{20} = 1.37508$.

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[3] Zawidski, *Z. physik. Chem.*, 35,129 (1900).

[4] Dolezalek and Schulze, *Verhandl. deut. physik. Ges.*, 14, 1091 (1912); Schulze, *ibid.*, 15,488 (1913); *Physik. Z.*, 14,922 (1913).

n-**Heptane.**—Material obtained from the Ethyl Gasoline Corporation was found to require no purification; m. p. −90.5°; b. p. 98.4°; d_4^{20} = 0.6838; n_D^{20} = 1.38767.

Carbon Tetrachloride.—The best product obtainable from Merck was dried over fused calcium chloride and distilled. A fraction boiling constantly at 76.4° was employed; b. p. 76.4'; n_D^{20} = 1.46026.

n-Butyl Chloride.—A material of good quality obtained from the Eastman Kodak Company was refluxed gently for half an hour over an equal volume of concentrated sulfuric acid, distilled, washed with water until free of sulfate, dried over fused calcium chloride and fractionated. A fraction boiling from 77.3 to 77.6° was employed; n_D^{20} = 1.40173.

Ethyl Bromide.—A material obtained from the Eastman Kodak Company was washed several times with cold, concentrated sulfuric acid, then with water until all sulfate was removed, dried over fused calcium chloride and fractionated. The fraction boiling at 38.3–38.4° was employed. Two lots thus prepared gave values of 1.42403 and 1.42408 for the refractive index; d_4^{20} = 1.4586; n_D^{20} = 1.42405.

Ethyl Iodide.—A material obtained from Merck was washed with a very dilute caustic potash solution until decolorized. Several drops of the caustic solution were added in excess and the material was then separated, thoroughly washed with water, dried over fused calcium chloride and fractionated. A fraction distilling without any perceptible change in temperature at 73.2° was employed. The vapor pressure of this material, 355.0 mm. at 50°, differs from Regnault's value 364.0 mm. given in Landolt-Bornstein, "Tabellen," but agrees satisfactorily with the more accurate value of Zawidski,[3] 353.4 mm.; b. p. 73.2°; d_4^{20} = 1.9292; n_D^{20} = 1.51330.

n-Butyl Bromide.—Material obtained from the Eastman Kodak Company was washed with cold concentrated sulfuric acid, then with sodium carbonate solution, dried over fused calcium chloride and fractionated. A fraction boiling from 100.4° to 100.6' was employed; n_D^{20} = 1.43984.

Ethyl Alcohol.—Ordinary 95% alcohol was refluxed over quicklime to which a small stick of sodium hydroxide was added. The refluxing was continued for 75–100

TABLE I

VAPOR PRESSURES OF PURE LIQUIDS (MM. OF HG)

t, °C.	Hexane	Ethyl iodide	Butyl chloride	Butyl bromide
20.0	...	...	31.3	82.3
30.0	186.1	162.6	51.0	130.2
40.0	275.7	244.8	52.2	198.5
50.0	400.6	355.0	126.7	295.8
60.0	568.0	505.9	189.6	420.7
70.0	...	...	271.3	591.4

t, °C.	Heptane	*t*, °C.	Carbon tetrachloride	*t*, °C.	Ethyl alcohol
22.7	41.4	19.2	88.0	22.7	51.8
30.0	58.2	32.4	156.0	32.6	90.1
30.3	58.8	41.2	222.8	35.7	105.6
38.4	86.0	50.0	312.0	41.8	145.1
50.0	141.1	60.8	452.8	57.2	306.8
51.2	150.0	68.7	586.4	59.6	342.7
61.2	220.0	76.4	760.0	69.4	531.1
69.5	297.8	..	...	78.1	747.6
70.0	301.4	..	...	78.4	760.0
79.5	419.7	..	...		
98.4	760	..	...		...

TABLE II

PARTIAL VAPOR PRESSURES OF BINARY MIXTURES (MM. OF HG)

(A) 50° (B)
Hexane–Heptane

B	p_A	p_B
0	400.6	0
0.1136	359.3	14.2
.2787	282.1	43.2
.3583	252.0	51.9
.4328	222.9	58.7
.5163	187.7	73.9
.6702	120.4	99.3
.8586	53.9	123.1
1.0000	0	141.1

(A) 50° (B)
Heptane–Butyl chloride

0	140.0	0
0.0496	135.2	17.2
.1128	129.4	37.8
.1580	118.9	63.9
.2870	105.5	96.2
.3853	93.9	123.7
.4462	85.6	143.4
.5273	72.4	167.2
.5955	63.8	184.4
.6386	57.6	197.6
.6979	50.4	212.1
.7797	39.5	231.7
.8645	25.2	255.0
.9565	11.5	277.3
1.0000	0	294.2

(A) 50° (B)
Carbon Tetrachloride–Heptane

0	308.5	0
0.0351	301.5	2.6
.1008	279.7	15.7
.1874	254.2	28.2
.2677	231.9	39.2
.3504	206.9	50.0
.4300	183.9	60.8
.4988	162.6	69.7
.5676	142.4	78.3
.6431	120.4	87.0
.6976	104.9	93.8
.8286	59.8	114.2
.9017	34.5	125.3
.9668	11.7	135.0
1.0000	0	140.5

(A) 50° (B)
Heptane–Ethyl iodide

B	p_A	p_B
0	141.1	0
0.0672	131.6	35.7
.1095	124.8	64.2
.1692	116.4	92.4
.2253	108.1	119.9
.3116	99.5	154.1
.3793	90.8	180.1
.4277	85.1	196.2
.4993	80.2	215.3
.5119	76.4	222.4
.5791	72.6	236.5
.6641	60.8	260.1
.7696	47.8	285.8
.8272	39.9	301.2
.8783	37.6	309.4
.9426	16.3	336.3
.9805	6.3	347.7
1.0000	0	354.1

(A) 50° (B)
Butyl chloride–Butyl bromide

0	295.8	0
0.0501	276.5	5.4
.1380	250.9	16.8
.2498	217.2	32.5
.3280	194.3	41.8
.4222	167.2	53.4
.4878	151.3	58.2
.5009	145.7	61.4
.5481	126.9	72.8
.6334	100.5	83.5
.7082	83.4	90.1
.7554	70.6	95.8
.8226	50.0	103.5
.8924	27.9	113.6
.9583	10.7	120.9
1.0000	0	126.7

(A) 30° (B)
Heptane–Ethyl iodide

B	p_A	p_B
0	58.2	0
0.0927	54.6	27.3
.1628	50.9	42.6
.2458	47.5	58.1
.2965	44.4	69.6
.3548	42.1	79.3
.4134	39.5	87.9
.4836	37.0	95.9
.5281	33.4	103.5
.5738	31.9	109.0
.6124	31.6	112.1
.7056	24.2	125.6
.7743	20.9	133.7
.8325	17.4	140.6
.8892	12.8	147.1
1.0000	0	161.8

(A) 30° (B)
Ethyl bromide–Ethyl iodide

0	560.9	0
0.0406	538.2	3.8
.0895	509.6	13.9
.1445	479 8	24 4
.2096	442.0	36.7
.2579	**411.7**	46.4
.3131	384 0	56.0
,3557	358.7	64 3
.3941	334.2	72.4
.4327	312.5	79.8
.4683	292.7	87.0
.4948	274.2	92.5
.5523	242.3	103.6
.5786	226.9	108 9
.6103	207.6	114.6
.6419	190.5	119.7
,6615	180.9	123.0
.7027	159.1	129.2
.7402	136.9	133.8
.8253	97.0	136.5
.8693	73.7	148.3
.9161	35.1	155.5
1.0000	0	161.8

TABLE II *(Concluded)*

(A) Heptane–	50° Butyl	(B) bromide
B	P_A	P_B
0	140.0	0
0.1171	125.8	19.6
.2362	110.6	37.8
.3329	98 4	51.1
.4323	86.1	62.8
.5182	74.8	72.6
.5836	66.4	80 0
.6333	59 6	85.9
.6588	57.3	87.5
.7123	49 0	94.5
.7935	37.2	102 6
.8805	23.3	112 2
.9521	9 6	121.2
0	0	127.0

(A) Heptane–	30° Ethyl	(B) bromide
B	p_A	p_B
0	58.0	0
0.0923	55.7	66.3
.2176	48.6	151.1
.2843	44.1	195.7
.3246	43 4	217 6
.4621	34 9	302 2
.4723	34.0	306 3
.6219	26 7	377.3
.7985	17.4	456 8
.9540	7.5	536.4
1.0000	0	567.8

(A) Hexane–	30°	(B) Heptane
B	P_B	p_B
0	186.1	0
0.1136	163 9	7.1
.2012	147.4	11.4
.3583	118 5	21.4
.4328	103.7	26.1
.5314	84.8	31.5
.6320	65.2	38.9
.6953	52.7	42 3
.8339	27.6	50.1
1.0000	0	580

hours, the lime being renewed four or five times. An exceptionally good quality of powdered lime was finally used and the material distilled off; b. p. 78.4–78.5°; n_D^{20} = 1.36130.

n-Butyl Alcohol.—Material obtained from the Commercial Solvent Corporation was refluxed over lime and twice fractionated. A fraction boiling between 117.1 and 117.2" was employed; n_D^{20} = 1.39942.

Results

The vapor pressures of several pure liquids are given in Table I and in Table II are the partial vapor pressures of the binary mixtures. In a system A–B the less polar liquid is, as a rule, designated as A, but where there is no polarity or little difference in polarity, other considerations may determine the order. For each system the column under B gives the mole fraction of component B in the mixture and the columns under p_A and p_B give the partial pressures of components A and B over the mixture.

Langmuir[1] has employed the principle of independent surface action to derive the following expressions for the partial vapor pressures of a mixture of two liquids, A and B

$$p_A = P_A A e^{S_A \varphi \beta^2/kT} \text{ and } p_B = P_B B e^{S_B \varphi \alpha^2/kT} \qquad (1)$$

in which p_A and p_B are partial pressures of Components A and B, respectively; P_A and P_B are vapor pressures of the pure liquids A and B, respectively; A and B are mole fractions of components A and B; S_A and S_B are surface areas of molecules of A and B; a and β are surface fractions of Components A and B

$$\alpha = \frac{S_A A}{S_A A + S_B B} \text{ and } \beta = \frac{S_B B}{S_A A + S_B B} \qquad (2)$$

k is the Boltzmann constant = 1.372 × 10^{-16}; T is the absolute temperature; and φ the "mixture energy," is a constant, dependent upon the molecular surface energies and independent of concentration.

For a mixture of two liquids, A and B, the molecules of one of which substances are enclosed by two kinds of surface, A and C, those of the other being enclosed by surfaces B and D

$$\varphi = ab\gamma_{ab} + ad\gamma_{ad} + bc\gamma_{bc} + cd\gamma_{cd} - ac\gamma_{ac} - bd\gamma_{bd} \tag{3}$$

in which a and c are the fractions of the surface of molecule A which are A-surface and C-surface, respectively, and b and d are the fractions of the surface of molecule B which are B-surface and D-surface, while γ_{ab} is the energy per sq. cm. of interface between surfaces A and B, γ_{ad} is the energy per sq. cm. of interface between A and D, etc.; φ is shown to be the energy per sq. cm. of molecular surface required for the transfer of a molecule of A from pure liquid A to pure liquid B or for the transfer of a molecule of B from pure liquid B to pure liquid A. The somewhat hypothetical surface areas of the molecules, expressed in square Ångstroms (10^{-16} cm.^{2}) are calculated from the densities by supposing that the liquids consist of close-packed spheres and the fractions of molecular surface, a, b, c, etc., used in the present paper are estimated from a comparison of the values of $V^{2/3}$ for the different groups, where V is the molar volume of the group at the boiling point of the liquid. It is assumed that the areas of the different kinds of surfaces in contact with one another are proportional to the fractions of the molecular surfaces involved, thus being calculable on the basis of a random orientation of the molecules. The value of γ for a certain kind of surface in a molecule is regarded as independent of the nature of the rest of the molecule, Thus γ should be the same for a hydrocarbon surface whether it be that of the heptane molecule or of the ethyl group in the ethyl alcohol molecule or of the butyl group in butyl chloride. Similarly, the energy per sq. cm. at a chlorine–hydrocarbon interface should be the same whether the chlorine is in carbon tetrachloride or butyl chloride, and whether the hydrocarbon is in another butyl chloride molecule or an alcohol or a heptane molecule. For binary mixtures in which fewer kinds of surface are involved, Equation **3** is simplified by the elimination of some of the terms, as will appear when it is applied to the results of the present investigation, in which only two or three kinds of surface are generally involved. This makes it possible to calculate the values of γ when φ is obtained for different mixtures.

Equation 1 may be written in the form

$$\varphi = 2.303\frac{kT}{S_A\beta^2}\log\frac{p_A}{P_AA} \text{ and } \varphi = 2.303\frac{kT}{S_B\alpha^2}\log\frac{p_B}{P_BB} \tag{4}$$

and used to calculate the value of φ, which, if the assumptions of the theory were rigidly correct, should be constant and the same for both partial pressure curves. Since the values of φ are greatly affected by experimental error, particularly at the ends of the partial pressure curves, it has seemed best to interpolate the values of p_A and p_B at intervals of 0.1 in the mole fraction and, for the sake of comparison, to designate the values of

φ calculated from the one partial pressure curve as φ_A and those from the other curve as φ_B. In Table III the first column gives the mole fractions of Component B from 0.1 to 0.9, and the succeeding columns give, for different systems, the values of p_A/p_AA and p_B/p_BB and the values of φ calculated from them. The deviations of p_A/p_AA and p_B/p_BB from 1 measure the deviations of the mixtures from Raoult's law.

TABLE III

VALUES OR p_A/P_AA, p_B/P_BB AND φ

	(A) 50° (B) Carbon tetrachloride–heptane				(A) 50° (B) 50° Heptane–butyl chloride			
	P_A = 308.5		P_B = 140.5		P_A = 140.0		P_B = 294.2	
B	p_A/P_AA	p_B/P_BB	φ_A	φ_B	p_A/P_AA	p_B/P_BB	φ_A	φ_B
0.1	1.008	1.068	1.89	0.25	1.032	1.156	1.15	0.57
.2	1.014	1.068	.86	.34	1.044	1.156	2.41	.71
.3	1.028	1.043	.81	.30	1.060	1.132	1.90	.77
.4	1.040	1.015	.68	.15	1.071	1.095	1.45	.75
.5	1.057	0.996	.65	− .01	1.092	1.074	1.17	.86
.6	1.077	.996	.64	− .02	1.124	1.053	1.05	.92
.7	1.107	.991	.68	− .08	1.178	1.055	1.05	1.05
.8	1.110	.992	.46	− .19	1.250	1.018	1.07	1.20
.9	1.151	.996	.64	− .32	1.358	1.012	1.05	2.94

	(A) 30° (B) Heptane–ethyl bromide				(A) 50° (B) Heptane–butyl bromide			
	P_A = 58.0		P_B = 567.8		P_A = 140.0		P_B = 127.0	
0.1	1.034	1.285	5.22	1.21	1.014	1.402	5.80	1.42
.2	1.078	1.221	4.64	1.08	1.028	1.299	2.79	1.34
.3	1.132	1.196	4.06	1.22	1.047	1.237	1.98	1.38
.4	1.149	1.180	3.48	1.42	1.072	1.165	1.58	1.29
.5	1.241	1.133	2.90	1.41	1.103	1.114	1.41	1.27
.6	1.293	1.080	2.32	1.24	1.143	1.075	1.28	1.27
7	1.322	1.039	1.74	1.00	1.214	1.048	1.31	1.41
.8	1.379	1.009	1.16	0.49	1.300	1.016	1.29	1.03
.9	1.550	0.990	0.58	−1.94	1.428	0.998	1.33	−0.12

	(A) 50° (B) Heptane--ethyl iodide				(A) 30° (B) Ethyl bromide---ethyl iodide			
	P_A = 141.1		P_B = 354.1		P_A = 560.9		P_B = 161.8	
0.10	.984	1.680	−1.79	2.54	0.9964	1.051	−1.37	0.25
.2	.997	1.524	−0.09	2.42	.9962	1.082	−0.37	.50
.3	1.019	1.413	1.08	2.42	.9933	1.092	− .29	.75
.4	1.063	1.313	1.82	2.40	.9806	1.128	− .43	1.39
.5	1.119	1.220	1.99	2.34	.9627	1.162	− .61	2.52
.6	1.204	1.139	2.10	2.19	.9538	1.149	− .53	3.66
7	1.345	1.082	2.28	2.17	.9508	1.130	− .42	5.82
.8	1.506	1.034	2.18	1.90	.9538	1.097	− .30	10.1
.9	1.758	1.008	2.17	1.66	.9449	1.058	− .28	24.1

The hexane–heptane mixtures are not included in Table III, because the linearity of the partial pressure curves shows that φ is 0. This supports the assumption involved in Langmuir's treatment that the energy, γ, between like surfaces, such as R–R, Br–Br, etc., is 0, since, for this system, Equation 3 simplifies to $\varphi = \gamma_{\text{R-R}}$ and $\varphi = 0$. The butyl chloride–butyl bromide mixtures are omitted from Table III because of the approximation of their curves to linearity and the heptane–ethyl iodide results at 30° are

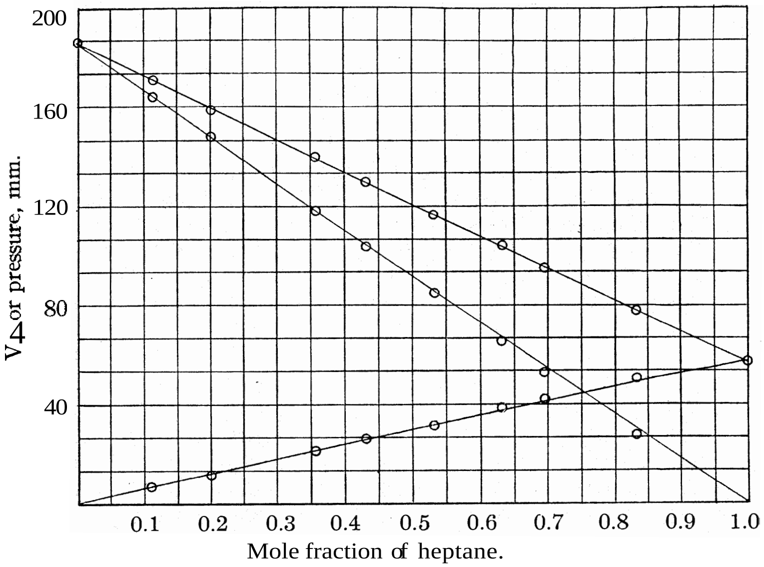

Fig. 2.—Hexane (A)–heptane (B) at 30°.

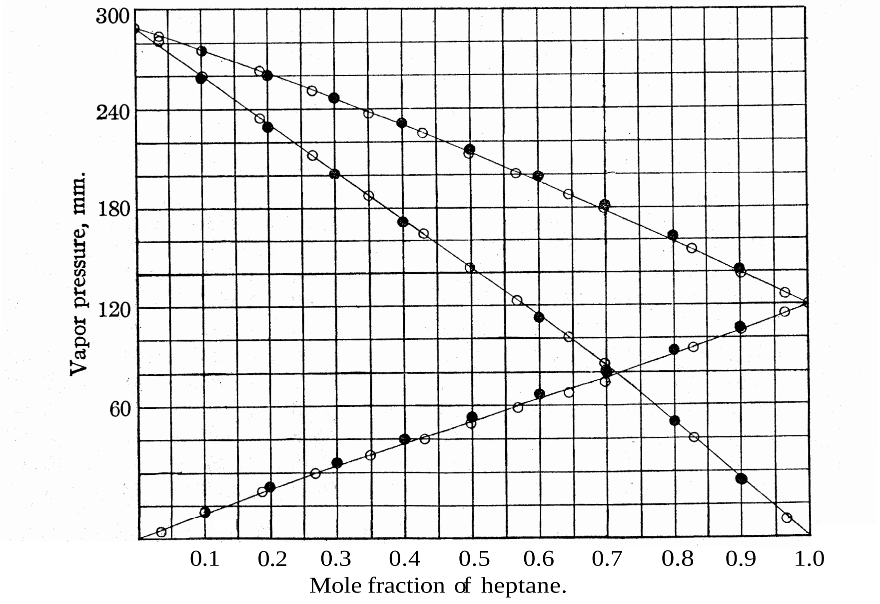

Fig. 3.—Carbon tetrachloride (A)–heptane (B) at 50°.

also omitted because of their resemblance to those at 50°, the values of φ at **30** and 50° differing by no more than the probable error. The results

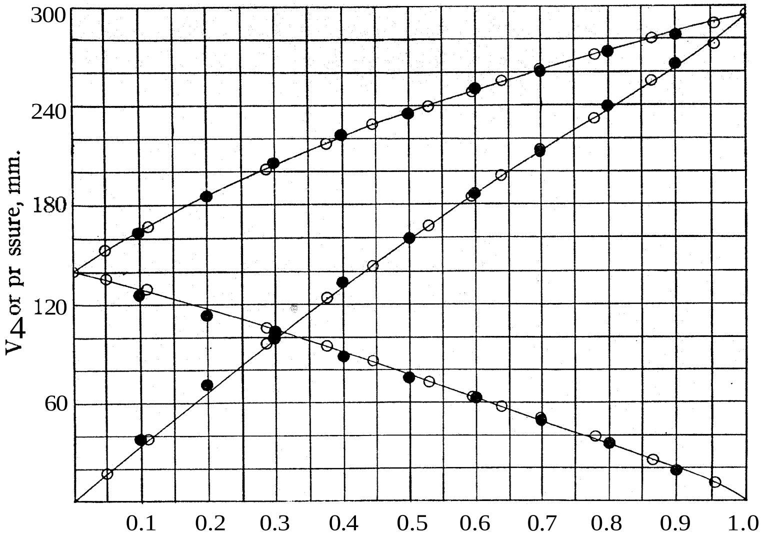

Fig. 4.—Heptane **(A)-butyl** chloride (B) at 50°.

are represented graphically in Figs. 2–9, in which the vapor pressures in mm. of mercury are plotted as ordinates against the mole fractions of

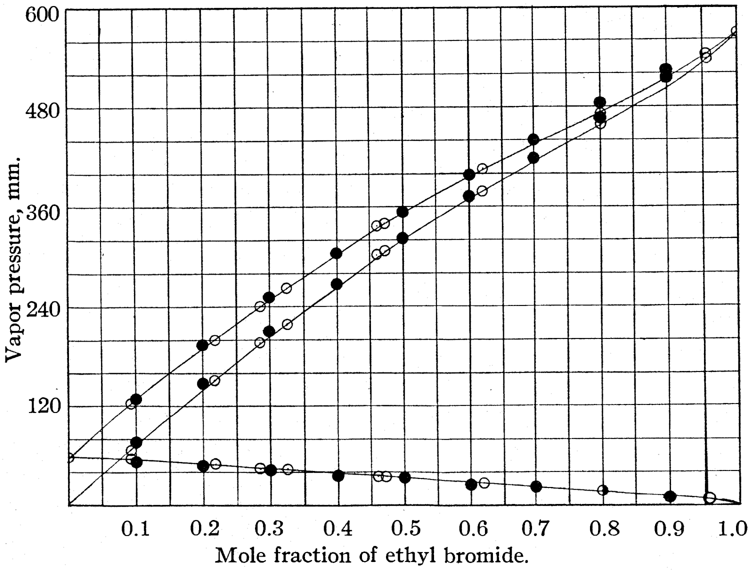

Fig. 5.—Heptane (A)-ethyl bromide (B) at 30°.

Component B as abscissas. The total pressure curve is, of course, uppermost and the partial pressure curve of Component B starts at the lower left-hand corner, while that of A starts at the lower right-hand corner. The experimental points are shown as hollow circles and the points calculated from φ as filled circles. Where the vapor pressure curves are straight, φ being 0, no calculated points are shown as they would obviously fall on the straight experimental lines. In the ethyl bromide–ethyl iodide system (Fig. 9) the departure from linearity is so slight as to render uncertain the value of φ, which is small in most of the mixtures and dependent upon concentration, as indicated by the curve in which the values of φ obtained from the pressures of the ethyl iodide are plotted as ordinates, shown at the right of the diagram, against the mole fractions of ethyl iodide as abscissas. In spite of the smoothness of this curve, great importance cannot be attached to it because φ is calculated from such small deviations.

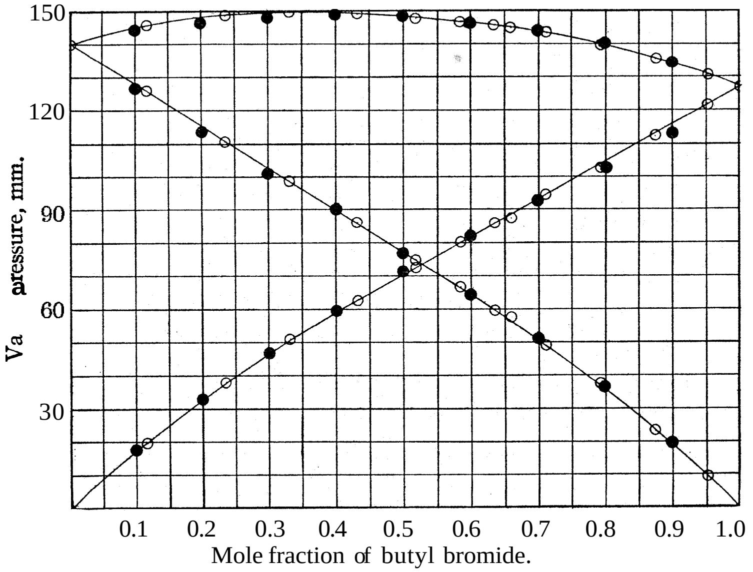

Fig. 6.—Heptane (A)–butyl bromide (B) at 50°.

Since the values of φ calculated from individual vapor pressures are subject to a considerable variation, φ may advantageously be obtained by plotting the values of $\log p_{\text{A}}/p_{\text{A}}A$ in Equation 4 as ordinates against those of β^2 as abscissas, or of $\log p_{\text{B}}/p_{\text{B}}B$ against those of α^2. If φ is constant, a straight line is thus obtained, the slope of which, when divided by $S_{\text{A}}/2.303kT$ or $S_{\text{B}}/2.303kT$, as the case may be, gives φ. The curves thus obtained for the heptane-ethyl iodide system show a tendency toward **a** slight deviation from linearity to give a curve with a point of inflection.

This deviation from linearity tends to increase with increasing difference in the polarity of the components. However, the curves are approximately linear for the systems heptane–butyl bromide, heptane–butyl chloride and heptane–carbon tetrachloride, and show no great deviation for heptane–ethyl bromide, although here the curvature is more pronounced. The curves for the ethyl bromide–ethyl iodide system show no approach to linearity, so that no constant value of φ can be obtained to use in calculating γ. The value of φ for hexane–heptane is 0 and for butyl chloride–butyl bromide so small as to be indistinguishable from 0. These values of φ are used to calculate the values of γ shown in Table IV, in which the

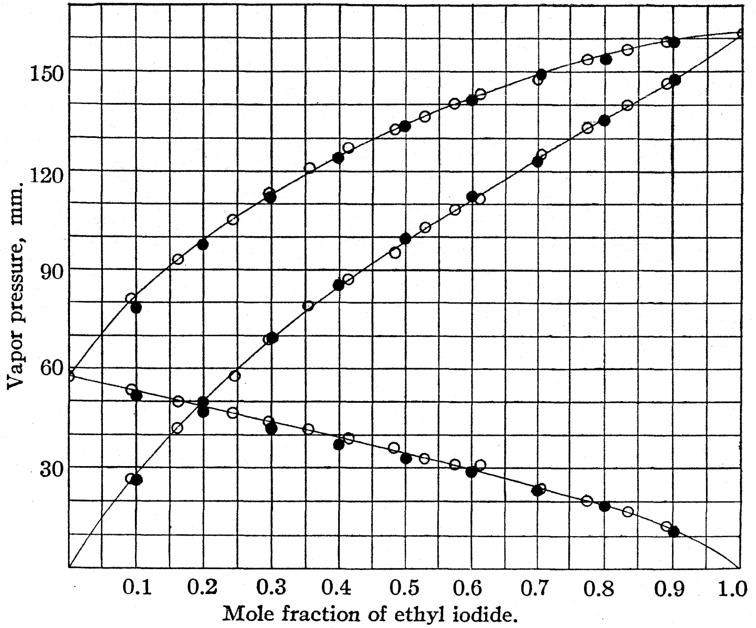

Fig. 7.—Heptane (A)–ethyl iodide (B) at 30°.

TABLE IV

VALUES OF SURFACE ENERGY, γ

Substance	Surface area (A^2)	Inter-face	System	φ	γ (ergs./cm.^{2})	γ (ergs./cm.^{2}) Langmuir
C_7H_{16}	154	R-CI	C_7H_{16}-CCl_4	0.6	0.6	4.1
C_4H_9Cl	123	R-Cl	C_7H_{16}-C_4H_9Cl	1.14	10.0	
C_2H_5Br	99	R-Br	C_7H_{16}-C_2H_5Br	1.6	6.8	10.0
C_4H_9Br	125	R-Br	C_7H_{16}-C_4H_9Br	1.36	9.2	
C_2H_5I	104	R-I	C_7H_{16}-C_2H_5I (30°)	2.52	7.9	13.7
Cl	41.5	R-I	C_7H_{16}-C_2H_5I (50°)	2.29	7.2	
Br	48.1	CI-Br	C_4H_9Cl-C_4H_9Br	0+	0+	
I	58.8	Cl-I		..	..	4.1

last column gives, for comparison, the values estimated by Langmuir. The molecules or radicals and their areas used in the calculation of the sixth column are shown in the first two columns. The calculation of the areas is, at best, a rough approximation, but, when the arbitrary character of the whole method of employing the molecular areas is considered, it becomes evident that the values assigned can have little significance as absolute quantities.

The value of γ_{R-Cl} determined from the heptane–carbon tetrachloride system should be the most accurate value in Table IV, for only two kinds

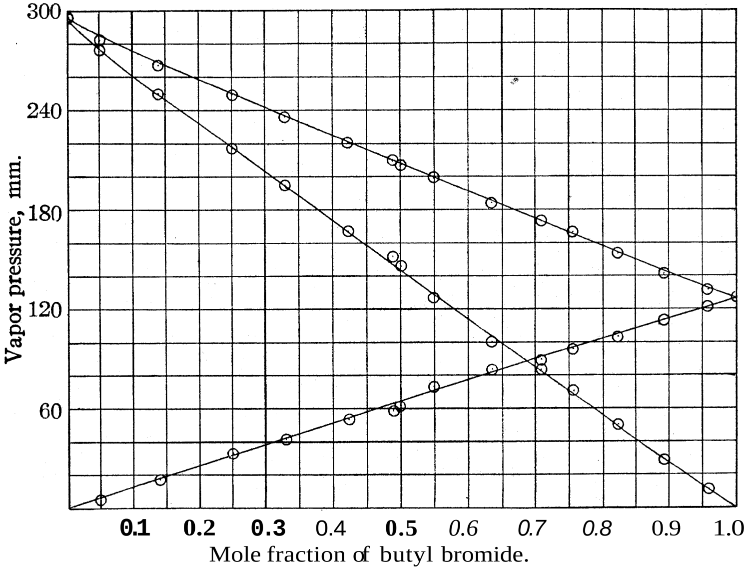

Fig. 8.—Butyl chloride (A)–butyl bromide (B) at 50°.

of surface being involved in the system, Equation 3 simplifies to $\varphi = \gamma_{R-Cl}$, thus eliminating the doubtful fractions of surfaces. The value of γ_{R-Cl} determined from the heptane–butyl chloride system is very dependent upon the surface areas used, as shown by the fact that, when surface areas consistent with those of Langmuir are taken, a value of 37.0 is obtained instead of 10.0. It is certain that the great difference between the value of γ_{R-Cl} obtained from the carbon tetrachloride–heptane system and that from the heptane–butyl chloride system can be due only in part to experimental error or the use of incorrect surface areas, and must, therefore, be attributed to a more fundamental cause. The values of γ_{R-I} obtained from the heptane–ethyl iodide system, because of the different surface areas used, differ from Langmuir's figure which, in this one case, could be calculated directly from experimental data. When the values of the surface areas used by Langmuir are employed, good agreement is obtained at

30°. For the system butyl chloride–butyl bromide, φ is only approximately 0 and one can, therefore, say only that $\gamma_{\mathrm{Cl-Br}}$ is small, presumably lower than Langmuir's value of 4.1 for $\gamma_{\mathrm{Cl-I}}$, as the surface energy between chlorine and bromine might be expected to be less than that between chlorine and iodine.

These systems show linearity, in some cases very approximate, when $\log p_{\mathrm{A}}/p_{\mathrm{A}}A$ is plotted against β^2 and $\log p_{\mathrm{B}}/p_{\mathrm{B}}B$ against α^2, and the experimentally determined vapor pressures may be satisfactorily reproduced by the use of a single value of φ, in spite of the considerable variation shown by the individual values of φ in Table III. The definitely established difference between the value of $\gamma_{\mathrm{R-Cl}}$ obtained from the heptane–carbon tetrachloride system and that from the heptane–butyl chloride system is significant since it indicates that the energy between surfaces is not always dependent only upon the kinds of surface involved, thus showing that the principle of independent surface action is limited in its applicability. The carbon tetrachloride molecule has no electric moment, while the butyl chloride molecule contains a large dipole.[5] The superposition of the forces of the dipole upon those of the chlorine surface presumably causes $\gamma_{\mathrm{R-Cl}}$ as measured for the heptane–butyl chloride mixtures to be different from the energy between hydrocarbon and chlorine surfaces where no dipole is present. As these are dipoles of the same order of magnitude present in the other alkyl halides here studied, it is probable

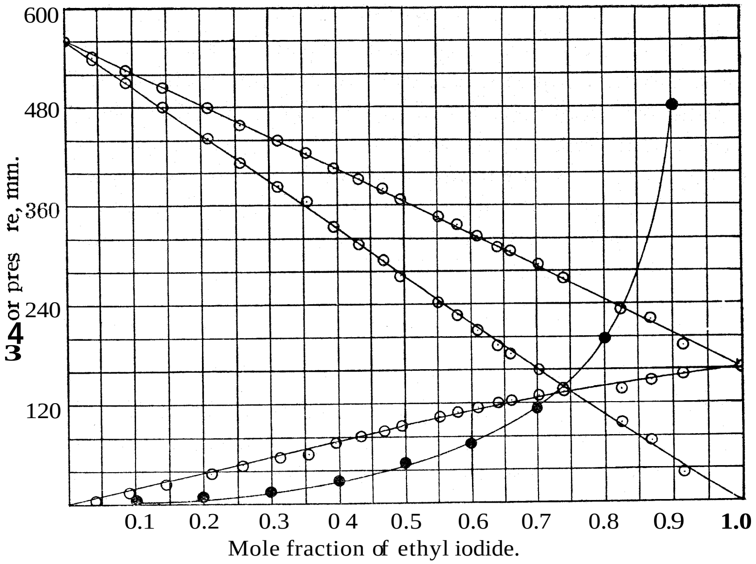

Fig. 9.—Ethyl bromide (A)–ethyl iodide (B) at 30°.

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[5] Smyth, *Chem. Reviews* (1929).

that the values of γ obtained from these systems are all influenced more or less by the fields due to these dipoles, which may also affect the results by bringing about molecular orientation. It is apparent that the lack of generality of the principle of independent surface action and the frequent absence of random orientation, as well as the uncertainty in estimating surface areas, prevent the accurate determination of absolute values for the surface energies and limit the applicability of the theory. These results will be further discussed in a subsequent paper, where they will be contrasted with the behavior of systems containing an alcohol as one component.

Summary

An apparatus is described for the measurement of the partial vapor pressures of binary liquid mixtures by a dynamic method. The pressures of eight different combinations of supposedly normal liquids and of several of the pure components are tabulated.

The data are used to examine Langmuir's theory of molecular surface energies, which is found to have an approximate applicability. Deviations from the theoretical behavior are ascribed to the presence of electric doublets in the molecules.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

MOLECULAR ORIENTATION AND THE PARTIAL VAPOR PRESSURES OF BINARY LIQUID MIXTURES. II. SYSTEMS CONTAINING AN ALCOHOL

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The apparatus described in Part I was used to determine the partial pressures of six different binary systems containing an alcohol as one of the components. The purification of the materials and the values of the physical constants used as criteria of their purity have been given in Part I.[1] Because of the somewhat different behavior of these systems containing an alcohol, it has been deemed advisable to treat them in a separate paper and contrast the results with those given by the supposedly normal liquids discussed in Part I. The experimentally determined partial pressures, p_A and p_B, of the components A and B are recorded in Table I, the composition of the mixtures being given in terms of the mole fraction B of the alcohol. The values of the partial pressures are interpolated graphically at intervals of 0.1 in the mole fraction of B and used to calculate the values of p_A/p_AA, p_B/p_BB, φ_A and φ_B, as was done in Part I,[2] the results

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[1] Smyth and Engel, THIS JOURNAL, 51, 2646 (1929).

[2] *See* Langmuir, "Third Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York, 1925, p. 3.

being recorded in Table II. In Figs. 1–6 the vapor pressures in millimeters of mercury are plotted as ordinates against the mole fractions B as abscissas. The total pressure curve is uppermost and the partial pressure curve of the alcohol starts at the lower left-hand corner, while that of the other component, A, starts at the lower right-hand corner. The values of φA and φB are plotted as ordinates on the same diagrams against those of B as abscissas, the points being indicated by filled circles.

TABLE I

PARTIAL VAPOR PRESSURES OF BINARY MIXTURES (MM. OF HG)

(A) 30° (B)
Heptane–ethyl alcohol

B	p_A	p_B
0	58.2	0
0.0400	56.0	22.0
.0684	56.4	47.2
.1236	56.4	56.1
.2803	54.8	62.9
.3342	54.5	63.5
.5151	54.0	65.9
.5934	51.8	68.1
.7174	49.9	69.7
.7687	47.9	71.0
.8154	43.5	73.5
.8550	40.6	73.9
.8902	32.1	79.2
.9173	18.4	87.9
.9545	10.1	87.0
.9913	4.7	77.8
1.0000	0	78.2

(A) 50° (B)
Heptane–ethyl alcohol

B	p_A	p_B
0	141.1	0
0.0514	132.3	111.9
.1180	133.6	155.8
.3022	130.5	176.9
.4382	130.0	181.3
.5862	126.6	184.7
.6646	121.5	188.0
.7327	120.0	191.3
.7720	114.9	193.9
.8230	106.2	198.6
.8788	71.8	221.8
.9274	47.2	234.5
.9769	21.6	225.8
1.0000	0	220.0

(A) 70° (B)
Heptane–ethyl alcohol

B	p_A	p_B
0	301.4	0
0.0567	265.9	234.4
.1180	274.5	339.8
.1573	272.8	375.2
.2575	275.8	413.8
.3633	274.3	431.6
.4290	269.7	442.4
.5069	269.0	446.7
.5968	267.0	450.7
.6648	259.6	458.1
.7174	252.4	465.3
.8689	251.0	462.8
.8200	245.6	459.3
.8640	227.9	465.5
.8940	183.1	493.4
.9250	129.5	522.3
.9564	83.0	527.0
.9827	44.9	524.5
1.0000	0	539.1

(A) 50° (B)
Heptane–butyl alcohol

0	140.5	0
0.0688	135.6	13.8
.1047	132.5	19.0
.1980	130.0	21.2
.2212	130.1	21.2
.3641	126.6	22.0
.5310	115.9	26.0
.5429	114.9	25.8
.6369	108.5	25.1
.6400	109.0	26.9
.6805	105.5	26.1
.7388	94.2	29.3
.7834	77.5	36.0
1.0000	0	33.3

(A) 50°
Carbon tetrachloride–
(B)
Butyl alcohol

0	308.9	0
0.0245	303.9	5.1
.1128	291.5	13.1
.2236	280.4	15.7
.3286	270.0	15.6
.4164	256.7	18.2
.5051	240.7	19.4
.5241	236.0	18 6
.6153	213.6	19.7
.6839	189.5	20.5
,7408	161.3	20.2
.8234	125.3	21.1
.8648	99.2	22.4
.9218	62.4	23.9
1.0000	0	33.3

(A) 30° (B)
Ethyl bromide–ethyl alcohol

0	567.8	0
0.1175	527.1	40.7
.2810	503.0	49.2
.2997	502.2	47.1
.4166	474.2	51.6
.5431	447.9	53.5
.6210	415.8	59.1
.6784	389.6	60.9
.7547	338.2	64.0
.7562	339.8	63.8
.8086	292.6	65.8
.8553	240.2	68.4
.8663	223.8	67.6
.8956	183.8	69.5
1.0000	0	78.4

TABLE I *(Concluded)*

(A) 50° (B)			(A) 30° (B)		
Butyl bromide–butyl alcohol			Ethyl iodide–ethyl alcohol		
B	p_A	p_B	B	p_A	p_B
0	127.0	0	0	162.3	0
0.1455	116.6	15.8	0.0438	162.4	25.9
.2140	113.6	17.3	.1307	152.9	44.9
.2594	111.2	18.4	.2886	148.2	53.1
.2815	109.6	19.0	.3668	145.3	55.3
.3898	104.9	20.9	.4000	144.4	56.2
.5033	97.6	22.4	.4875	139.8	57.1
.5226	97.1	21.9	.5507	137.3	59.6
.5790	92.5	22.7	.6259	132.1	61.8
.6368	86.2	23.3	.6854	125.8	63.3
.7093	78.7	24.3	.7384	116.7	64.9
.7751	67.5	25.3	.7836	106.5	66.2
.8832	43.3	27.2	.8195	97.4	68.4
.9383	26.3	27.9	.8483	88.2	69.4
.9739	16.2	27.5	.8912	72.1	70.0
1.0000	0	33.3	.9519	32.1	70.7
			1.0000	0	78.2

The partial pressure curve of ethyl alcohol in the heptane–ethyl alcohol system (Fig. 1) shows a small but well-defined rise to a maximum near B = 0.94. The phenomenon was at first attributed to a repeated error in the

TABLE II

VALUES OF p_A/P_AA, p_B/P_BB AND φ

	(A) 30° (B)				(A) 50° (B)			
	Heptane–ethyl alcohol				Heptane–ethyl alcohol			
	P_A = 58.2		P_B = 78.2		P_A = 141.1		P_B = 220.0	
B	p_A/P_AA	p_B/P_BB	φ_A	φ_B	p_A/P_AA	p_B/P_BB	φ_A	φ_B
0.1	1.069	6.778	55.8	10.7	1.053	6.727	47.4	11.2
.2	1.192	3.900	34.1	8.71	1.178	3.818	32.5	9.02
.3	1.350	2.685	22.8	7.45	1.336	2.667	23.0	7.76
.4	1.561	2.062	17.0	6.67	1.536	2.057	17.3	6.95
.5	1.856	1.688	13.4	6.17	1.814	1.673	13.7	6.39
.6	2.277	1.449	11.0	6.04	2.232	1.409	11.3	5.86
.7	2.921	1.270	9.52	6.04	2.882	1.227	9.58	5.51
.8	3.952	1.151	7.88	6.99	3.969	1.114	8.30	5.59

	(A) 70° (B)				(A) 50° (B)			
	Heptane–ethyl alcohol				Heptane–butyl alcohol			
	P_A = 301.4		P_B = 539.1		P_A = 140.5		P_B = 33.3	
0.1	1.018	5.832	(15.9)	10.8	1.060	5.560	29.6	8.13
.2	1.145	3.673	28.0	9.14	1.164	3.300	18.3	6.58
.3	1.308	2.542	22.3	7.71	1.303	2.201	13.4	5.37
.4	1.511	2.022	17.3	7.08	1.505	1.726	10.9	4.76
.5	1.778	1.655	13.8	6.50	1.715	1.441	8.19	4.33
.6	2.196	1.391	11.5	5.90	2.023	1.247	7.45	3.84
.7	2.856	1.203	9.90	5.14	2.410	1.157	6.37	4.23
.8	4.114	1.062	8.88	4.88				

TABLE II (*Concluded*)

(A) 50° (B)
Carbon tetrachloride–butyl alcohol
P_A = 308.9 P_B = 33.3

B	p_A/P_AA	p_B/P_BB	φ_A	φ_B
0.1	1.064	3.605	21.3	6.18
.2	1.141	2.250	13.3	4.96
.3	1.258	1.600	10.2	3.70
.4	1.398	1,275	8.30	2.62
.5	1.560	1.081	7.02	1.19
.6	1.760	0.926	6.15	−1.82
.7	1.953	.841	5.31	−7.22
.8	2.170	.754	4.68	−26.4
.9	2.522	.767	4.44	−98.5

(A) 30° (B)
Ethyl bromide–ethyl alcohol
P_A = 567.8 P_B = 78.4

B	p_A/P_AA	p_B/P_BA	φ_B	φ_B
0.1	1.041	4.580	22.8	9.06
.2	1.130	3.180	16.8	8.49
.3	1.248	2.125	13.1	6.96
.4	1.409	1.690	1 . 1	6.37
.5	1.609	1.453	9.51	6.35
.6	1.875	1.275	8.44	6.22
.7	2.230	1.146	7.63	6.00
.8	2642	1.052	6.85	4.85
.9	3.170	0.993	6.19	−1.33

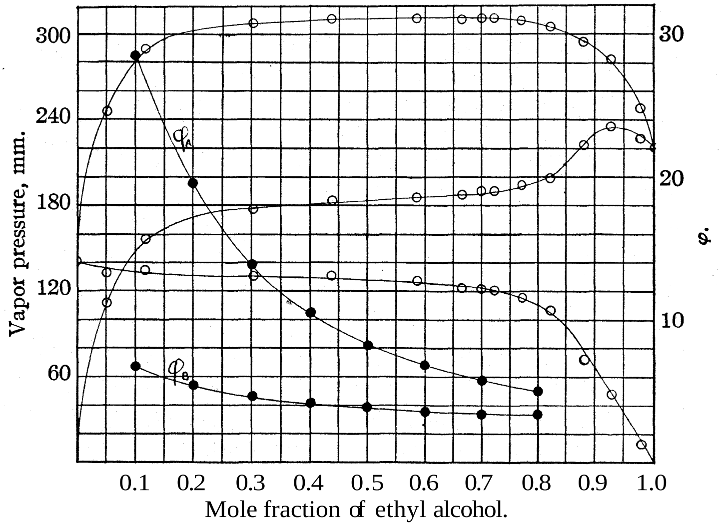
(A) 50° (B)
Butyl bromide–butyl alcohol
P_A = 127.0 P_B = 33.3

B	p_A/P_AA	p_B/P_BB	φ_A	φ_B
0.1	1.042	3.694	17.8	6 2 2
.2	1.126	2.628	12.4	5.70
.3	1.238	1.952	9.77	5.05
.4	1.382	1.577	8.16	4.58
.5	1.555	1.321	6.98	3.95
.6	1.779	1.152	6.20	3.05
.7	2.073	1.030	5.64	1.10
.8	2.480	0.946	6.26	−4.70
.9	2.953	.918	4.85	−30.8

(A) 30° (B)
Ethyl iodide-ethyl alcohol
P_A = 162.3 P_B = 78.2

B	p_A/P_AA	p_B/P_BA	φ_B	φ_B
0.1	1.068	5.115	41.1	9 6 5
.2	1.163	3.601	22.6	8.36
.3	1.301	2.293	16.8	7.45
.4	1.473	1.790	13.4	6 82
.5	1.716	1.491	11.4	6.48
.6	2.067	1.300	10.3	6.37
.7	2543	1.169	9.24	6.43
.8	3.173	1.071	8.35	6.04
.9	4.190	1.009	7.79	3.09

analysis, but careful checking of the method of analysis eliminated this possibility. The rise is found to decrease with rising temperature, which may be expected to reduce abnormalities arising from molecular association



Pig. 1.—Heptane (A)–ethyl alcohol (B) at 50°.

or intermolecular action. No such maximum appears in the curves for the mixtures of ethyl alcohol with other substances than heptane, but in the heptane–butyl alcohol system (Fig. 2), the beginning of a rise is indicated from B = 0.7 to B = 0.8 which might lead to a maximum in the neighborhood of B = 0.9. Unfortunately, however, this region could not be investigated as the butyl alcohol mixtures containing a little heptane bumped so violently, apparently because of an abnormally high surface tension, that the vapor pressures could not be measured. It appears that some complex formation may occur in this region of the heptane–alcohol mixtures, but the dielectric behavior of the mixtures shows no irregularity in this region and an attempt at explanation is unwise until more definite knowledge is obtained.

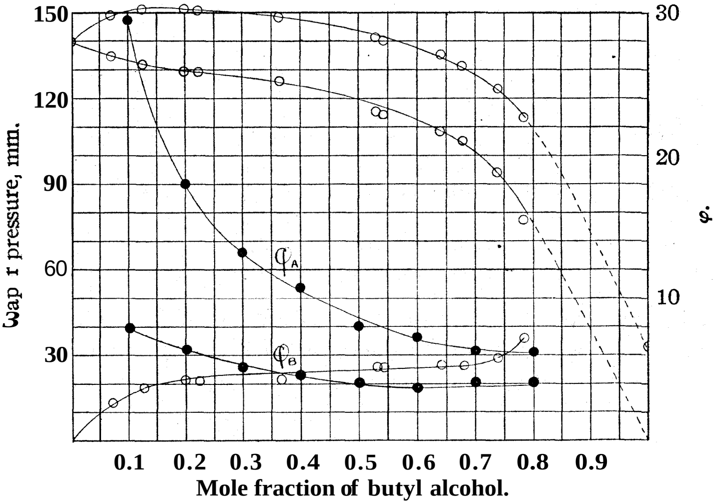


Fig. 2.—Heptane (A)–butyl alcohol (B) at 50°.

Table II shows that these systems deviate much more from Raoult's law than do the normal liquids considered in Part I, the value of p_B/P_BB for B = 0.1 in the heptane (A)–ethyl alcohol (B) system at 30° being 6.778 as compared to the theoretical 1 of Raoult's law. The deviation of the partial pressure of a component from Raoult's law increases with decreasing concentration of the component. The values of φ are larger and vary more widely than those for the mixtures in Part I. Indeed, the variation of φ is so great that it is impossible to select a value from those in Table II for *a* system with any expectation of reproducing the partial pressures from it.

As an illustration of the manner in which a single value of φ fails to reproduce the experimentally observed vapor pressures, Fig. 4 shows as partly filled circles the pressures for the ethyl bromide-ethyl alcohol system, calculated by means of the **Langmuir** equation, the value of φ being taken from Table III as 5.88. A similar failure in the calculation of the pressures has been found to occur in the other systems. The calculated points are, however, omitted from the other figures in order to avoid too great complication of the diagrams.

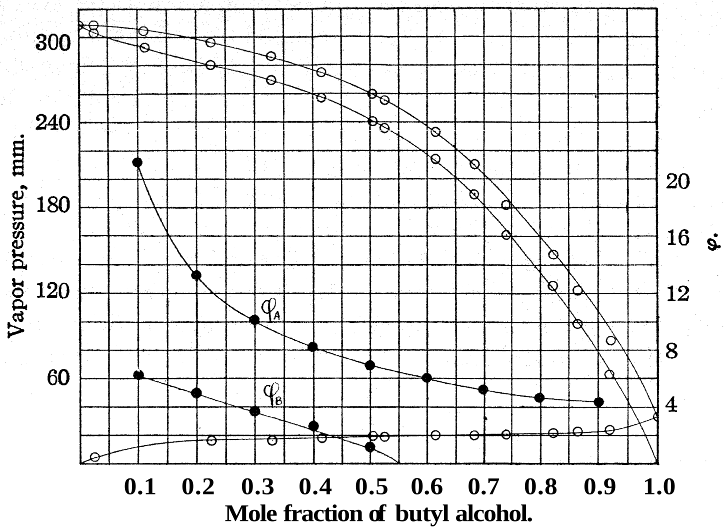


Fig. 3.—Carbon tetrachloride (A)-butyl alcohol (B) at 50°.

If $\log p_A/P_AA$ is plotted against β^2 and $\log p_B/P_BB$ against α^2, straight lines are not obtained, as should be the case if φ were constant. When log

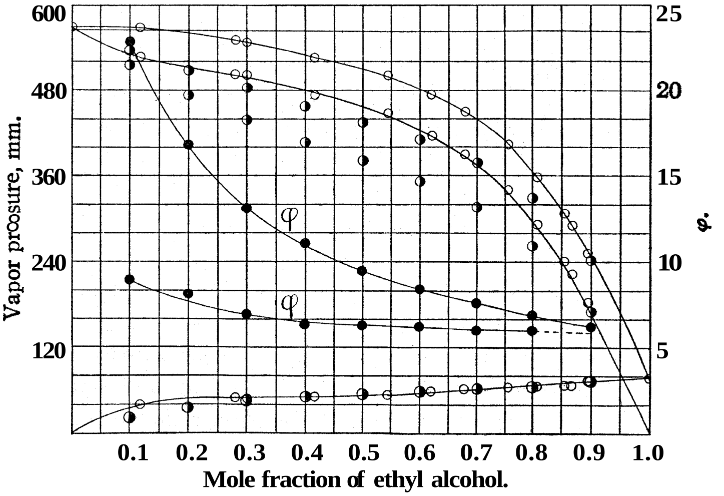


Fig. 4.—Ethyl bromide (A)-ethyl alcohol (B) at 30°.

$(\log(p_A/P_AA))$ is plotted against $2 \log \beta$ and $\log(\log(p_B/P_BB))$ against $2 \log \alpha$, portions of the curves obtained are linear and average values of φ

are calculated from these portions. The curves for the two components give somewhat different values of φ, but the values from the curves for the non-alcoholic components which are constant over a wider concentration range will be used in discussion.

For the sake of comparison, all the values are given in Table III together with the values of the surface energy calculated from them, the values of γ from Part I being used when necessary in the calculation. The first column gives the interface for which γ is calculated, the second column the temperature at which the vapor pressures were determined, the third under A gives the component from the partial pressures of which the values of φ in the fourth column are obtained and the values of γ calculated from them are in the fifth column. The sixth column under B gives the alcohol from the partial pressures of which the values of φ and γ in the remaining columns are calculated. At the foot of the table are given the values of γ used in calculating the surface energies for the halogen–hydroxyl interfaces, together with the surface areas (in square Ångströms) not previously used in Part I.

TABLE III

VALUES OR φ AND γ FOR SYSTEMS CONTAINING AN ALCOHOL

Interface	t, °C.	A	a	γ	B	a	γ
R–OH	30	C_7H_{16}	5.77	68 2	C_2H_5OH	7.05	83.3
R–OH	50	C_7H_{16}	6.1	72.4	C_2H_5OH	7.6	89.9
R–OH	70	C_7H_{16}	6 78	80.2	C_2H_5OH	8.67	102 5
R–OH	50	C_7H_{16}	4 7	97.7	C_4H_9OH	6.4	133 1
CI–OH	50	CCl_4	4 0	101.6 (80.8)	C_4H_9OH	7.25	95.7
Br–OH	30	C_2H_5Br	5.88	64 9	C_2H_5OH	8.34	81.8
Br–OH	50	C_4H_9Br	4.47	108 9 (92 4)	C_4H_9OH	6.65	134.6 (118.2)
I–OH	30	C_2H_5I	6.85	70 0	C_2H_5OH	6 67	68.9

Areas: OH = 24.7; C_2H_5OH = 849; C_4H_9OH = 112.5. Values of γ used in calculations: R–OH = 73.7 for C_2H_5OH; 97.7 for C_4H_9OH (but values in parentheses are calculated from R–OH = 73.7); R–C1 = 0.6; R–Br = 6 8 for C_2H_5Br, 9.2 for C_4H_9Br; R–I = 7 9.

Possessed of the same uncertainties as the values obtained in Part I, these results are rendered more difficult of interpretation by the greater effect of molecular orientation in the mixtures. The energy at an interface where an hydroxyl group is involved is evidently so large in comparison with the energies at the other interfaces that the orientation of the alcohol molecules relative to one another must be more important in determining the behavior of the system than their orientation relative to the molecules of the other component or the orientation of the molecules of the other components relative to one another. For example, in an ethyl bromide–ethyl alcohol mixture at 30°, if an hydroxyl surface is in contact with bromine, γ is 64.9, if in contact with hydrocarbon, γ is 68.2, but, if in contact with another hydroxyl, y is 0, while, if a bromine surface is in contact with hydrocarbon, y is 6.8 as compared to 0 when the bromine is in contact with another bromine.

It is evident that when a butyl compound is used to obtain γ, the resulting value is higher than when an ethyl compound is used. Thus, the value of γ_{R-OH} at 50° is 72.4 when ethyl alcohol is used and 97.7 when butyl is employed and γ_{Br-OH} is 64.9 when the ethyl compounds are used and 108.9 in the butyl mixtures. Similarly, in Part I, it was found that the value obtained from the heptane–butyl bromide mixtures was higher than that from the heptane–ethyl bromide system. This difference could be largely eliminated by adjustment of the values of the surface areas, but, as these are derived by a consistent procedure from experimental data, their treatment as adjustable constants is not justifiable. The mean value $\gamma_{R-OH} = 73.7$ is used in calculation where ethyl alcohol is concerned and the value 97.7 for the mixtures containing butyl alcohol, but, for the sake of comparison, the value 73.7 is also used with the latter and the results thus obtained are shown in parentheses. It is safer to compare molecules with the same hydrocarbon chain. One may thus conclude from the values for the ethyl compounds that γ_{R-OH}, γ_{Br-OH} and γ_{I-OH} are not very different from one another and, similarly, from those for the butyl compounds, that γ_{R-OH}, γ_{Cl-OH} and γ_{I-OH} differ little from one another, and that all are much larger than those for the interfaces considered which do not contain hydroxyl. The values in Table III are not sufficiently accurate to warrant their arrangement in a definite order, but it may be concluded that γ_{R-OH}, γ_{Cl-OH} and γ_{I-OH} are of the same order of magnitude and are much larger than the values for the hydro-

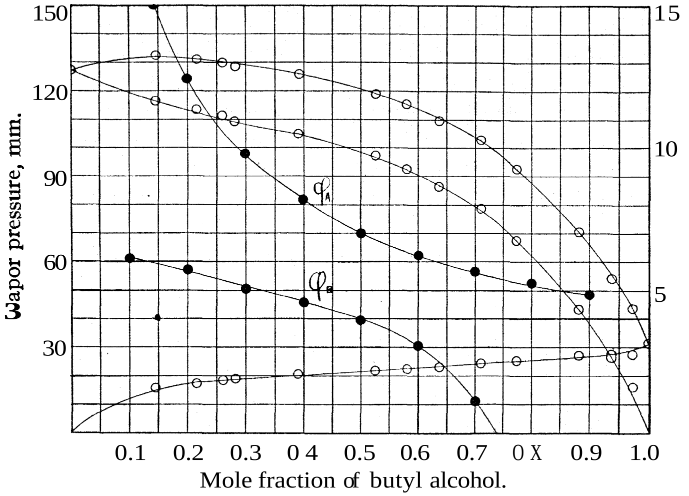


Fig. 5.—Butyl bromide (A)–butyl alcohol (B) at 50°.

carbon–halogen and halogen–halogen interfaces. The values of γ_{R-OH} and γ_{R-OH} are quite different from those of Langmuir, 33.7 and 49.6, respectively, but when Langmuir's value 33.7 is used for γ_{R-OH} instead of 73.7 in calculating γ_{Br-OH} from the data for the ethyl bromide-ethyl alcohol system, the value 49.5 is obtained, which shows how dependent these results are upon one another as well as upon the uncertain surface fractions.

Langmuir examined the effect of molecular orientation in a hexane–ethyl alcohol mixture by means of a necessarily approximate method and was misled by a numerical error to the belief that the effect was very slight, but concluded that it might be important in some liquids, particularly in those whose molecules act as dipoles. Consequently, a second term was introduced into the exponent of the original equation to take care of the energy of orientation in such liquids. When this equation is applied to these systems, a straight line is sometimes found but the frequent failure to obtain linearity shows that the equation is not generally applicable, although, of course, the mere presence of an additional adjustable constant renders it more capable of reproducing experimental data.

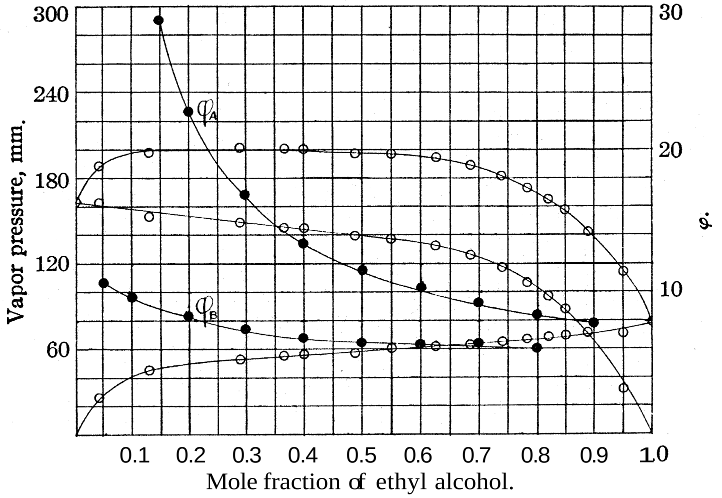


Fig. 6.—Ethyl iodide (A)–ethyl alcohol (B) at 30°.

A general explanation of the deviations of the mixtures from normal behavior may be given in qualitative terms. The field of force around a molecule due to a doublet in its interior depends not merely upon the electric moment of the doublet, but also upon its location in the molecule. Thus the diethyl ether molecule has an electric moment of 1.14×10^{-18} e.s.u.,[3] the resultant, presumably, of two dipoles located in the regions of

[3] Stuart, *Z. Physik*, 51,1490 (1928).

attachment of the ethyl groups to the oxygen atom. The ethyl groups serve as a shield for the dipoles and thus prevent the molecule from being surrounded by a strong field of force. Ether, consequently, behaves as a normal unassociated liquid, even measurements of dielectric polarization at room temperature failing to give evidence of interference of the molecular force fields with one another. The ethyl alcohol molecule has two somewhat similar doublets located in the regions where the ethyl group and the hydrogen are attached to the oxygen atom, the resultant moment[4] being 1.74×10^{-18}. The ethyl group may be pictured as partially screening one side of the molecule from the action of the doublets, but the doublets are close to the surface on the hydroxyl side of the molecule and a strong molecular field results. Alcohol, consequently, shows properties which cause it to be termed a highly associated liquid, and its dielectric behavior is abnormal in the extreme. The water molecule, of electric moment[3,5] 1.8×10^{-18}, possesses two doublets similar to those in the alcohol molecule, but has no ethyl group to serve as a screen. The resultant powerful molecular field renders water a strongly associated and very abnormal liquid. If the higher alcohols are considered, it is evident that with increasing size of the hydrocarbon chain, which contains no appreciable doublets, the doublets at the hydroxyl group will be more and more screened from those in neighboring molecules and the effects of their fields thereby reduced. Consequently, the alcohols become less abnormal with increasing molecular weight.

Ethyl bromide, in spite of the moment, 1.86×10^{-18}, possessed by its molecule, is ordinarily termed a normal liquid.[6] Its doublet should lie in the region of attachment of the ethyl group to the bromine atom and should thus be screened not only by the ethyl group but also by the large bromine atom, which should greatly reduce the molecular field as compared to that of the ethyl alcohol molecule. In ethyl iodide the screening effect of the large iodine atom should be greater than that of the bromine atom, and this, taken in conjunction with the slightly smaller moment of the molecule,[7] 1.67×10^{-18}, should give a smaller molecular field. In conformity with this the dielectric behavior of the two substances shows that the ethyl bromide molecules affect one another more strongly than do those of ethyl iodide. This effect is also apparent in the vapor pressures given in Part I, for the heptane-ethyl bromide system shows a somewhat greater variation in the values of φ, presumably as the result of orienting forces, than is found in the heptane–ethyl iodide system. Butyl bromide, in which the longer hydrocarbon chain should reduce the effect of the mo-

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[4] Stranathan, *Phys. Rev.*, 31, **653** (1928).

[5] Williams, *Physik.* Z., 29, *204* (1928).

[6] Smyth and Morgan, THIS JOURNAL, 50, 1547 (1928).

[7] **Value** recently obtained in this Laboratory by Mr. W. N. Stoops.

lecular dipoles upon one another, shows but slight variation in the value of φ, and the heptane–butyl chloride mixtures behave similarly.

It appears that the deviations of liquids from the behavior required by the Langmuir equation may be qualitatively explained in terms of the forces acting between the molecular dipoles. Forces which greatly restrict the freedom of orientation of the dipoles in an externally applied electric field may yet be insufficient to impair seriously the validity of the Langmuir equation. As the effects of the dipoles upon one another depend not only upon their electric moments but also upon their location in the molecules and upon the sizes and shapes of these molecules and probably upon the electronic constraints in them, it appears impossible to formulate any generally valid expression for the exact quantitative representation of the interaction of molecular dipoles. Evidently the assumptions upon which the Langmuir equation is derived are too simple to permit of its general and exact application, but the approximate agreement between the calculated and the observed results for the less polar liquids and the general trend of the surface energies calculated indicate that the theory bears a relation to fact beyond a mere resemblance of the equation to the Duhem thermodynamic equation, and the idea of molecular surface energies may lead to most interesting results in spite of the difficulties in its exact quantitative application.

The writers wish to express their indebtedness to Dr. Irving Langmuir for his kindness in discussing this work with one of them.

Summary

The partial vapor pressures of six binary liquid systems containing an alcohol as one component are measured. The results are found to deviate considerably from the behavior required by Langmuir's theory of molecular surface energies. The deviations are explained in terms of the interaction of the electric doublets contained in the molecules. It is concluded that, as this interaction is dependent upon not only the electric moments of the doublets but also their locations in the molecules and the sizes and shapes of these molecules and, probably, the constraints upon the electrons in them, no generally valid quantitative formulation of the effect is possible at present.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

THE CONDUCTANCE AND TRANSFERENCE NUMBER OF THE CHLORIDE ION IN MIXTURES OF SODIUM AND POTASSIUM CHLORIDES

BY DUNCAN A. MACINNES, IRVING A. COWPERTHWAITE AND THEODORE SHEDLOVSKY

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The transference numbers of the ion constituents in mixtures of sodium and potassium chlorides have been investigated by various workers, including Braley and Hall,[1] Schneider and Braley,[2] and Dewey.[3] In the first two papers mentioned the authors presented what they thought was evidence that there are ionic complexes in these mixtures. These conclusions were called in question by MacInnes[4] and Bjerrum,[5] who could find evidence, in the experimental work, for simple ions only. This conclusion was later accepted by Braley and Rippie[6] on repeating some of the experimental results of Schneider and Braley.

The question of ionic complexes has been raised again by McBain and Van Rysselberge.[7] They have concluded from transference number measurements made on 0.05 N salts containing divalent ions, to which rather large amounts of salts had been added, that complex ions occur in such mixtures.

Since the moving boundary method appears to be capable of greater precision than the Hittorf method, at least as usually carried out, it seemed desirable to test the applicability of the method in the case of mixtures. Purthermore, it seemed possible that, since McBain and Van Rysselberge's work, if confirmed, indicates large amounts of complexes in the solutions they worked with, precise measurements might show at least a small amount in mixtures of potassium and sodium chlorides.

It is not, however, possible, with the moving boundary method, to determine the separate transference numbers of the two positive ion constituents in these mixtures. The determinations were therefore carried out on the chloride ion constituent, which is common to both salts. The measurements described below are on the transference numbers and conductances of mixtures of potassium and sodium chlorides at a total (volume) concentration of 0.1 N, at 25°.

Theoretical

If we let x represent the proportion of potassium chloride in the mixture

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[1] Braley and Hall, THIS JOURNAL, 42, 1770 (1920).

[2] Schneider and Braley, *ibid.*, 45, 1121 (1923).

[3] Dewey, *ibid.*, 47, 1927 (1925).

[4] MacInnes, *ibid.*, 47, 1922 (1925).

[5] Bjerrum, *Kgl. Danske Videnskab. Selskab., Math. fys. Medd.* [vi] 9, 3 (1925).

[6] Braley and Rippie, THIS JOURNAL, 49, 1493 (1927).

[7] McBain and Van Rysselberge, *ibid.*, 50, 3009 (1928).

of potassium and sodium chlorides, the transference number T_{Cl} of the chloride ion will be

$$T_{\text{Cl}} = \frac{\Lambda_{\text{Cl}}}{x\Lambda_{\text{K}} + (1 - x)\,\Lambda_{\text{Na}} + \Lambda_{\text{Cl}}} \tag{1}$$

This formula assumes that we are dealing with solutions containing only simple ions. If the equivalent conductances Λ_{Cl}, Λ_{K}, Λ_{Na} of the ion constituents are independent of the values of x, or, in other words, if the mobilities of the ions are the same in the various mixtures as they are in the solutions of the pure salts at the same total salt concentration, the equivalent conductance of the mixtures should vary linearly with values of x. This, we will see below, is nearly but not exactly true. Since it follows from these assumptions, and has been found experimentally, that for these solutions $N\Lambda_{\text{KCl}} = N'\Lambda_{\text{NaCl}} = \Lambda_{\text{Cl}}$, in which N and N' are the transference numbers of the chloride ion for 0.1 N solutions of pure potassium and sodium chlorides, Equation 1 can be put in the form

$$T_{\text{Cl}} = \frac{N\Lambda_{\text{Cl}}}{x(1 - N)\Lambda_{\text{KCl}} + (1 - x)(1 - N')\Lambda_{\text{KCl}}\,N/N' + N\Lambda_{\text{KCl}}} \tag{2}$$

which can readily be rearranged to

$$T_{\text{Cl}} = \frac{N'}{x\left(\frac{N'}{N} - 1\right) + 1} \tag{3}$$

which gives the transference numbers of the chloride ion in the mixtures in terms of the transference numbers of the pure salts. Any large deviation from values of transference numbers in mixtures computed from Equation 3 would tend to indicate the presence of complexes in the solutions.

Experimental

The Moving Boundary Measurements.—The technique of the moving boundary measurements followed that described in previous papers.[8] The only substantial addition to the procedure is an automatic device for initially forming the boundary. Since, as may be recalled, the rate of motion of the boundary was found to be influenced by vibration, the apparatus was placed in a thermostat which was mounted on a modified Julius suspension. The weakness of this arrangement was, however, that the initial turning of the plate-glass disks over each other in forming the boundary could not be carried out while the vibration-free support was effective. It was necessary to extend the springs so that the thermostat rested on a table, after which the disks could be turned by hand. Vibrations could thus disturb the boundary at its moment of formation, and there was a possibility of further disturbance on releasing the springs. Although recent work has shown that the result of slight mixing or diffusion is overcome, in time, by the potential gradients acting around the boundary,[9] an occasional run showed

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[8] (a) MacInnes and Smith, THIS JOURNAL, **45**, 2246 (1923); (b) Smith and MacInnes, *ibid.*, 46, 1398 (1924); (c) MacInnes and Brighton, *ibid.*, **47**, 994 (1925); (d) Smith and MacInnes, *ibid.*, **47**, 1009 (1925); (e) MacInnes, Cowperthwaite and Blanchard, *ibid.*, **48**, 1909 (1926); (f) MacInnes, Cowperthwaite and Huang, *ibid.*, 49, 1710 (1927).

[9] MacInnes and Cowperthwaite, *Proc. Nat. Acad. Sci.*, *15*, *18* (1929).

variations which indicated more mixing than could be rectified in this manner. It was, therefore, decided to make the boundary formation take place without disturbing the vibration support. The arrangement adopted is shown in Fig. **1.** In order to form the boundary the electrode tube **A** must swing around the pivot P until the lower opening of **A** is directly over the measuring tube D. This is accomplished by means of the spring S which is mounted on the upright of the support. By means of a sprocket, E, and chain the motion of this spring is transmitted to the upper disk B carrying the electrode vessel **A.** The chain carries a projection which fits into a hole in the disk. The procedure for forming a boundary is as follows. After filling the measuring tube and electrode vessel as described in previous papers, the disks are placed approximately as shown in the figure. The spring S is then given a number of turns by means of the milled head and is locked with the pin Q. The chain is next adjusted over the sprocket and disk and the pin Q is raised. This causes the disk B to swing through a small angle so that the edge of the sector I is resting against the projection of the rod R through the guide K. The whole apparatus is then placed in the thermostat on the vibration-free support and electrical connection is made to the electrodes and to the terminals of the solenoid M. Now if the circuit is closed through this solenoid the rod R is raised and the disk turns until the projection H encounters the edge of the guide K and the electrode vessel **A** is directly over the tube D. The projection H is arranged eccentrically around the screw fastening it to the brass sector I in order that the final position of the disk B can be adjusted exactly. Due to the viscosity of the lubricant between the two glass disks the turning takes place smoothly with no jerk at the end. The procedure as described causes a sharp boundary to form between the solution under investigation in the measuring tube D and the "indicator" solution in the electrode vessel **A.**

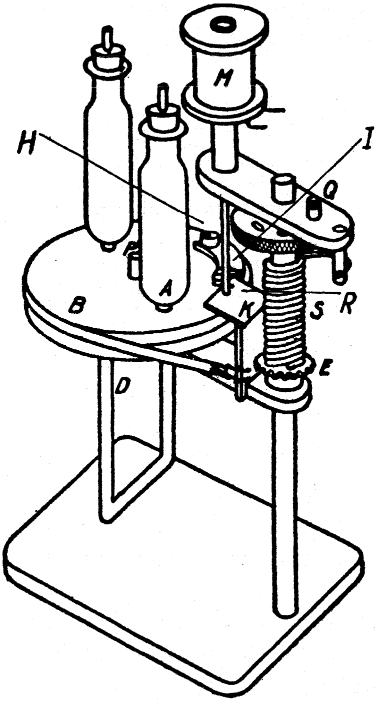

Fig. 1.

The Results of the **Moving** Boundary Experiments.—As already stated the transference numbers measured in this series of determinations were those of the chloride ion in potassium chloride–sodium chloride mixtures. As "indicator" solutions mixtures of potassium and sodium acetates were used, having in each case the same ratios of the positive ion constituents. Surrounding the silver–silver chloride electrode in the (closed) cathode chamber was a strong solution of potassium acetate. The results of the transference number measurements are given in Table I. It will be seen that for each proportion of potassium chloride the transference number obtained is independent of the indicator concentration, within the range studied, showing that adjustment was obtained in each case. This observation is supported by an earlier series of determinations which were made in order to test the possibility of measurements of the type here described. In this earlier series the range of indicator concentrations was still wider than that given in Table I. It should, further, be emphasized that each transference number in the table is the average of six figures rarely if ever differing more than 0.1% from the average. Each of these figures is the result of a measurement in which the boundary has moved eight or more centimeters.

TABLE I

TRANSFERENCE NUMBERS OF CHLORIDE ION IN 0.1 *N* POTASSIUM CHLORIDE–SODIUM CHLORIDE MIXTURES AT 25°

Transference number	Indicator concn.	Transference number	Indicator concn.	Transference number	Indicator concn.
0.25 Potassium Chloride		0.50 Potassium Chloride		0.75 Potassium Chloride	
0.5839	0.068	0.5560	0.064	0.5311	0.068
.5838	.068	.5557	.066	.5313	.070
.5828	.068	.5566	.066	.5314	.072
.5832	.068	.5560	.068		
.5831	.070				

The figures in Table I have been corrected for the volume change at the electrode as described by Lewis.[10] This correction is —0.0009 and —0.0002 to the observed transference numbers of pure 0.1 *N* sodium and potassium chloride solutions. The values for the mixtures have been interpolated from these figures.

The Conductance Measurements.—Conductance measurements were made on the solutions whose transference numbers had been determined, as well as on the 0.1 N solutions of the pure salts. Since it is intended to describe the bridge used in these measurements in some detail in a later article, only the more essential facts concerning the results will be given here. The Washburn pipet cell used was calibrated with "demal" solution prepared as described by Parker and Parker.[11] The resistance box used was calibrated against a box which had been standardized by the Carey Foster method against B. of S. standard resistances. During the measurements the cell was placed in an oil thermostat, a description of which will also be deferred. This maintained a constant temperature within 0.002°, as shown by a platinum-resistance thermometer.

The results of the measurements are given in the appropriate column in Table II. We feel that all variables that may affect the accuracy of these measurements have been controlled at least within 0.02%. Our A values for the pure salts (106.69 for NaCl and 128.86 for KCl) are not far from the values (106.71 and 128.82, respectively) given in Noyes and Falk's[12] compilation, which are based on Bray and Hunt's, and Melcher's

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[10] Lewis, THIS JOURNAL, 32, 862 (1910).

[11] Parker and Parker, *ibid.*, 46, 312 (1924).

[12] Noyes and Falk, *ibid.*, 34, 454 (1912).

work. The latter figures have been corrected for a change of —0.14% in the constants used in calibrating the cells since Parker and Parker[1'] have shown that Kohlrausch's value for the conductance of the 0.1 N calibrating potassium chloride solution used by these authors is in error by that amount. For the mixtures the only earlier conductance work with which comparison can be made is that of Stearn,[13] which is not of sufficient accuracy for our purpose.

Preparation of Solutions and Purification of Material. -The solutions were prepared on a volume normal basis, *i. e.*, 0.1 mole of the fused salt, or mixture of salts in the desired proportions, in a liter of solution at 25°, in carefully calibrated pyrex volumetric flasks, using conductivity water. The best obtainable samples of potassium and sodium chloride were first crystallized from concentrated solution with hydrogen chloride gas, after which they were recrystallized several times from conductivity water.

Discussion of Results

The results and conclusions of our measurements are outlined in Table II. In the second column, under the heading "transference numbers observed," are given the averages of the values from Table I, and also the transference numbers for the two pure salts from earlier moving boundary measurements. The next column contains the transference numbers of the mixtures as computed from Equation **3.** In the fourth and fifth columns are given the conductivity data for the pure salts and the mixtures, and also the conductance values computed on the basis of a simple linear variation of these values with the proportion of potassium chloride in the mixture.

TABLE II

TRANSFERENCE NUMBERS AND EQUIVALENT CONDUCTANCES OF 0.1 N KCL–NACL MIXTURES AT 25°

KCl, %	Transference numbers, T_{Cl} Observed	Transference numbers, T_{Cl} Computed	Equivalent conductance, Λ Observed	Equivalent conductance, Λ Computed	Chloride-ion conductance $T_{Cl}\Lambda$
0	0.6137	...	106.69	....	65.48
25	.5834	0.5832	112.13	112.23	65.42
50	.5563	.5553	117.67	117.78	65.45
75	.5313	.5309	123.25	123.32	65.48
100	.5080	...	128.86	....	65.46

In the last column will be found the product of the observed transference numbers and the observed conductances. If simple ions only are present this is the equivalent conductance of the chloride-ion constituent in the mixtures and in the pure salts. As can be seen, this product is a constant well within the experimental error. It is an interesting fact that the observed transference numbers are all slightly larger than the computed

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[13] Stearn, THIS JOURNAL, 44, 670 (1922).

values, whereas in the case of the equivalent conductances the reverse is true. This would follow if the chloride ion has the same mobility in the mixtures as in the solutions of the pure salts and one or both of the mobilities of the positive ions are slightly lowered in the solutions of the mixed salts. However, the effect, though definite, is all within 0.1%. There is, quite obviously, no evidence whatever of complex ions in these solutions.

Summary

An addition to the moving boundary apparatus for determining transference numbers is described, with the aid of which the boundary can be formed without disturbing the apparatus while it is mounted on a vibration-free support.

Transference numbers of the chloride-ion constituent in tenth-normal mixtures of sodium and potassium chlorides have been determined. Accurate conductance measurements have been made on the same solutions.

Within the experimental error chloride-ion conductance is the same in the mixtures as in the solutions of the pure salts. There is no evidence of complex ion formation.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE BAKER LABORATORY, CORNELL UNIVERSITY]

A LABORATORY OZONIZER

BY ALBERT L. HENNE

RECEIVED MARCH 28, 1929 PUBLISHED SEPTEMBER 5, 1929

It is of general knowledge that ozone is by far the most suitable reagent for the oxidation of double linkages; there is also a general impression that this method requires special and expensive equipment as well as a trained operator. The purpose of this note is to show that the method is exceedingly simple and to give practical information concerning the installation and the cost of the equipment.

L. I. Smith[1] has described an ozonizer which is very satisfactory from the stand-point of the ozone yield. The present apparatus is a simplification of that described by Smith. The purposes of the alterations were to eliminate the use of mercury, which renders the apparatus heavy, expensive and liable to breakage, to modify slightly the shape of the ozone tubes in order to simplify the glass-blowing and to allow the use of sulfuric acid as an electrode, to eliminate the litharge joints, which always have a tendency to expand and break the glass tubes and to render the building of the unit a much shorter and less complicated task. All these features substantially decrease the cost.

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[1] L. I. Smith. THIS JOURNAL, 47, 1844 (1925).

Figure 1, which shows one of the ozone tubes, is self-explanatory. A lead wire dipping in dilute sulfuric acid is used as one of the electrodes; the lead wire (six fuse-wires twisted together) remains straight and centered by virtue of its own weight, so that sparking is prevented. As in the apparatus of Smith, three tubes are sealed in series and almost completely immerged in a bath of water in a battery jar. The water is used as a second electrode and as a cooling medium. Since no mercury is used and since the weight of the tubes is nearly counterbalanced by the weight of the water displaced, it is unnecessary to have an elaborate device to maintain the tubes in position. All that is needed to support the weight is a plate of bakelite blocked 3 cm. from the bottom of the battery jar and fitted with slots to accommodate the lower extremities of the tubes. The lid of the battery jar is fitted with corresponding slots (except that the diameter of the holes is 4 cm. instead of 3.5 cm.); this is quite sufficient to maintain the tubes in position. The tension (10,000 v.) between the electrodes is furnished by a $^{1}/_{4}$-kw. transformer. The maximum cost of the whole outfit can be established as follows: transformer, \$10; battery jar, \$7; material and labor for three ozone tubes, \$10. A good glass-blower can make a tube in about an hour and a half, and spoils less than one tube out of four.

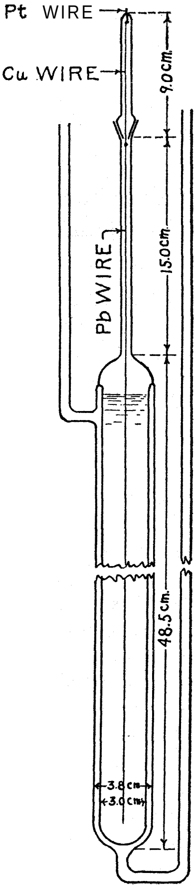

Fig. 1.

The operation of the ozonizer is essentially that indicated by Noller and Adams.[2] It should be remembered that complete drying of the oxygen is a very important feature. Despite the modifications, the yield of ozone is substantially the same as that indicated by Smith; the percentage weight of ozone will be about 14%, 8% and 3% when oxygen is delivered at the rate of 4, 20 and 100 liters per hour, respectively. This corresponds to an hourly output of 0.7, 3.6 and 4.6 g. of ozone.

The inexpensive material used for radio panels is suitable for the bottom plate and for the battery jar lid. A T2355 Thordarson transformer, type RS Cat. 135, and an Exide 21 X 31 × 42.5 cm., type I?-9, battery jar were used.

ITHACA, NEW YORK

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[2] Noller with Adams, THIS JOURNAL, 48, 1074 (1926).

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

STUDIES ON THE THERMOCHEMISTRY OF THE COMPOUNDS OCCURRING IN THE SYSTEM $CaO–Al_2O_3–SiO_2$. I. THE HEAT OF SOLUTION OF CALCIUM OXIDE IN HYDROCHLORIC ACID[1]

BY T. THORVALDSON, WELDON G. BROWN[2] AND C. R. PEAKER[2]

RECEIVED MARCH 28, 1929 PUBLISHED SEPTEMBER 5, 1929

The immediate reason for undertaking the work described in this paper was that a reliable value for the heat of solution of calcium oxide in hydrochloric acid was required for the calculation of the heats of formation of the calcium aluminates from the heats of solution of these substances.

The values obtained by Berthelot[3] and Thomsen[4] were 46.06 and 46.03 calories per mole of CaO, respectively. From three determinations (46.03, 46.14 and 46.33), Backstrom[5] arrived at the weighted mean 46.20 calories (24°) per mole for the heat of solution of calcium oxide in normal hydrochloric acid at 25°. For our calculations a value for the heat of solution in more dilute acid was required.

Apparatus

The calorimeter used was of the adiabatic type developed by Richards[6] and his collaborators with certain slight modifications. A gold calorimeter vessel was used and the stirring of the liquid in the calorimeter vessel was effected by a motor-driven rotary stirrer made of an alloy of 80% of gold and 20% of copper. The stirrer was insulated from its shaft by a rod of hard rubber. The shaft made an air-tight joint where it passed through the brass tube in the cover of the calorimeter jacket so that diffusion of air between the calorimeter and the environment was eliminated. The rate of stirring was controlled by an external resistance so as to be constant as shown by a revolution counter attached to the shaft of the stirrer. A rate of 290 revolutions per minute was found to be sufficient to prevent thermal stratification in the calorimeter. This rate gave a rise of temperature of 0.001° per minute.

Two series of determinations of the thermal leakage of the calorimeter under a thermal head of 0.010 ± 0.001° and 0.020 ± 0.001°, respectively, were made. After the system was in equilibrium (water equivalent, 600 cal.) the calorimeter stirrer was stopped for ten-minute intervals and then started again. In each case the rise in temperature due to thermal leakage during the ten-minute interval was less than 0.0005°.

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[1] The work described in this paper was made possible by bursaries awarded to Mr. Brown and Mr. Peaker by the National Research Council of Canada. The authors wish to express their appreciation of this assistance.

[2] This paper represents part of the theses presented by W. G. Brown and C. R. Peaker in partial fulfilment of the requirements for the degree of M.Sc. in Chemistry at the University of Saskatchewan.

[3] Berthelot, *Ann. chim. phys.*, [5] 4, 531 (1875).

[4] Thomsen, "Thermochemische Untersuchungen," 1883, Vol. 3, p. 247.

[5] Bäckström, THIS JOURNAL, 47, 2443 (1925).

[6] (a) Richards, Henderson and Forbes, *Proc. Am. Acad.*, **41,** 3 (1905); (b) Richards, Rowe and Burgess, THIS JOURNAL, 32, 1176 (1910).

The Beckmann thermometers employed had been calibrated at the U. S. Bureau of Standards. A careful comparison with a Beckmann thermometer which had been calibrated by one of us by a thermochemical method[7] gave an agreement within 0.001" over the whole range of the thermometer scale The actual centigrade temperatures were obtained by comparison with a calibrated standard, the ice-point being taken at the same time.

The large discrepancies often found between thermochemical results from different laboratories indicate the importance of the elimination of constant errors. It was therefore considered advisable to carry out some measurements of well-known thermochemical constants, with this apparatus, before proceeding with the determination of the heat of solution of calcium oxide. Two determinations were chosen: the first involving a temperature rise of 4°, *i. e.*, the neutralization of sulfuric acid using special vessels and solutions identical with those used by Richards and Rowe;[8] the second involving a very small rise of temperature (about 0.15") *i. e.*, the heat of dilution of $HCl\cdot 20H_2O$ to $HCl\cdot 200H_2O$ according to the method of Richards, Rowe and Burgess.[6b] In both cases the method of stirring described above was used.

A series of six determinations of the heat of neutralization of sulfuric acid gave the values 16,979, 16,997, 16,990, 16,972, 16,982 and 16,984 or a mean of 163,984 calories per $^1/_2$ H_2SO_4 at 20° as compared with 16,982 calories given by Richards and Rowe[8] Ten determinations of the heat of dilution of $HCl\cdot 20H_2O$ to $HCl\cdot 200H_2O$ gave a mean value of 552 calories per mole, the highest value being 556 and the lowest 549, as compared with 556 calories obtained by Richards, Rowe and Burgess,[6b] 549 calories reported by Richards and Rowe and 552 calories calculated from dilution results by Richards and Thorvaldson.[10] The agreement between the results is all that could be expected and indicates an absence of constant errors affecting the temperature measurements.

Materials

Hydrochloric Acid.—The purest acid of commerce was diluted and redistilled with a quartz condenser, the middle portion of the distillate being collected in quartz flasks. This was then diluted with water freshly redistilled with a block tin condenser and adjusted to $HCl\cdot 200H_2O$, the concentration being checked both by titration with pure sodium carbonate and by gravimetric determinations of chloride.

Calcium Oxide.—The procedure used for eliminating impurities from the calcium salts was essentially similar to that recommended by Richards and Hönigschmid.[11]

The water and the reagents used, such as acids, ammonia, ammonium carbonate and ammonium oxalate, were all purified by redistillation or recrystallization immediately before use. The calcium salts to be purified were in each case, to begin with, of the highest quality obtainable ("for analysis," "special," "analyzed"). The mother liquors were separated from the recrystallized products by means of high-speed power centrifuges. Precipitations of calcium carbonate and calcium oxalate were made from solutions containing 5 g. of CaO per liter. The precipitates were washed by decantation with large volumes of redistilled water, time being given for diffusion of impurities from the solid, and the final wash water was separated by aid of the centrifuge. Calcium oxide was finally obtained from the carbonate or oxalate by ignition in platinum crucibles in an electric muffle. While determinations of the heat of solution in hydrochloric acid were made on eighteen different samples of calcium oxide, the data recorded in this

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[7] Richards and Thorvaldson, THIS JOURNAL, **37,** 81 (1915).

[8] Richards and Rowe, *Proc. Am. Acad.*, *49,* 191 (1913).

[9] Richards and Rowe, THIS JOURNAL, 42,1632 (1920).

[10] Richards and Thorvaldson, *ibid.*, 44, 1057 (1922).

[11] Richards and Honigschmid, *ibid.*, 32, 1577 (1910).

paper in Table II represent the values obtained with four of the most carefully purified samples prepared from calcium salts from three widely different sources. Although the original materials contained only very small amounts of impurities, the process of purification in each case increased the heat of solution materially.

Sample A.—Calcium nitrate was recrystallized twice in vessels of fused silica. Calcium carbonate was then precipitated as calcite at room temperature with ammonium carbonate.

Sample B.—Calcium carbonate was dissolved in nitric acid. The neutral solution was treated with excess of bromine and milk of lime, boiled, filtered and the calcium nitrate recrystallized three times in vessels of fused silica. The calcium was precipitated as the carbonate by ammonium carbonate. The thoroughly washed and centrifuged calcium carbonate was dissolved in hydrochloric acid and precipitated as calcium oxalate.

Sample C.—A solution of recrystallized calcium chloride was treated with excess of bromine and milk of lime, boiled, filtered and changed to the nitrate by repeated evaporation with excess of nitric acid. The nitrate was then recrystallized five times in glass, three times in platinum vessels and the calcium precipitated as calcium carbonate (calcite) by ammonium carbonate.

Sample D.—A portion of the calcium nitrate obtained after the eighth recrystallization of Sample C was precipitated by ammonium carbonate at the boiling point, crystals of aragonite being obtained.

Experimental Procedure

The experimental technique of adiabatic calorimetry is well known[6,8,9,10] and will not be described here. The method of introduction of the calcium oxide into the calorimeter should, however, be described. The calcium oxide, freshly ignited to constant weight, was dropped into the calorimeter vessel through a glass tube which reached through the cover of the calorimeter jacket. To the lower end of the glass tube there was attached a tube of gold foil which just made contact with the surface of the liquid in the calorimeter. It was found that any spattering of the liquid was caught by the gold tube. As soon as the calcium oxide had been introduced the gold tube was released and dropped into the acid solution, where it was held suspended from the cover to prevent it from interfering with the stirrer. The glass tube was then removed and the weight of any lime adhering to its inner surface, which generally did not exceed two or three milligrams, was determined by titration with standard

TABLE I

HEAT CAPACITY OF THE SYSTEM

	Specific heat	Heat capacity, cal./deg.
600.4 g. $HCl \cdot 200H_2O$	0.9821[a]	589.65
195.9 g. gold calorimeter and foil	.031[b]	6.07
14.5 g. stirrer (80% Au, 20% Cu)	.044[b]	0.64
0.3 g. air ($^1/_2$ of total)	.240[b]	.07
Thermometer		1.40
Total heat capacity		597.8

[a] Richards, Mair and Hall, THIS JOURNAL, 51, 727 (1929).

[b] I. C. T., 1929, Vol. V, pp. 81, 92, 120.

acid. The original weight of calcium oxide was then corrected for the amounts remaining in the crucible and adhering to the tube. The calcium oxide dissolved very rapidly, a constant stirring correction being usually reached in from six to eight minutes. A thermal head of 0.010 ± 0.005° was maintained between the jacket and the calorimeter vessel during the experiments.

All weights were corrected to vacuum. The calcium oxide was introduced at the final temperature of the reaction (20") and is therefore not included in the heat capacity.

TABLE II

HEAT OF SOLUTION OF CaO IN $HCl \cdot 200H_2O$

Expt.	Sample of CaO	CaO, g.	Final temp., °C.	Temp. rise,[a] °C.	Heat of soln 18° cal per g. of CaO
1	A	2 9098	20.03	4 (36	829 2
2	A	2.8976	20.00	4 019	829 2
3	A	2.9352	20.05	4 C64	827 7
4	B	2.9410	20.13	4 072	827 7
5[b]	B	2.9155	19.95	3.976	828 9
6	B	2.8859	20.00	3.998	828 2
7	C	2.8870	19.97	3.998	827 8
8	C	2.8701	19.93	3.973	827.5
9	C	2.8609	19.95	3.965	828.5
10	C	2.8483	19.97	3.945	828.0
11	D	2.9703	19.98	4.121	829.4
12	D	2.9732	20.03	4.122	828.8
13	D	2.8974	20.06	4.024	830.2
14	D	2.7087	19.93	3.757	829.2
		Average	20.00	4.005	828.6

[a] These values are corrected for (1) stirring, (2) stem exposed, (3) setting of thermometer and (4) variation in temperature of CaO from 20° at time of introduction into the calorimeter.

[b] Heat capacity in Expt. 5 was 607.8 cal./deg.

Discussion of Experimental Results

The average value from Table II represents the isothermal heat of reaction at the final temperature 20.00°, expressed in terms of the mean calorie between 16 and 20".

One further correction should be applied to this value. The volume of air enclosed in the calorimeter system was about 500 cc., one-half of which was included in the calculated heat capacity of the system. Assuming that this volume of air was completely saturated with water vapor both at the beginning and at the end of an experiment, the heat absorbed by evaporation would be 1.1 calories, which is equivalent to approximately 0.4 calorie per gram of calcium oxide. As thermal equilibrium is attained rather rapidly at the end of the run, it would probably be more nearly correct to apply three-fourths of the calculated correction.

Applying a correction of 0.3 calorie per gram, the final value for the isothermal heat of solution of calcium oxide in $HCl\cdot 200H_2O$ at 20° becomes 828.9 calories per gram (mean calorie 16 to 20°). This is equivalent to 194.4 kj. or 46.50 $cal.^{20°}$ per mole.

The samples of calcium oxide used in Expts. 9 and 10 were heated at 1200" for three hours after being brought to constant weight in the usual way at 800 to 900°. In another case a sample was heated at 1200° for twenty-four hours without giving an appreciable change in the heat of solution. The results indicate that the heat of solution is not materially affected by the temperature of ignition between the limits 800 and 1200°.

Summary

The heat of solution of calcium oxide in $HCl\cdot 200H_2O$ at 20" was found to be 194.4 kilojoules or 46.50 $cal.^{20°}$ per mole. The heat of solution was found not to be materially affected by the temperature of ignition between 800 and 1200".

SASKATOON, CANADA

[CONTRIBUTION PROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 215]

THE IODOMETRIC DETERMINATION OF IRON

BY ERNEST H. SWIFT

RECEIVED APRIL 3, 1929 PUBLISHED SEPTEMBER 5, 1929

Introduction

In the course of an investigation the demand arose for a rapid, fairly accurate method of determining iron in a precipitate of ferric hydroxide. A review of the various volumetric processes for determining iron was therefore made. Oxidation methods, using standard permanganate or dichromate solutions, involve the preliminary reduction of the ferric solution. In the reduction methods solutions of stannous chloride or of a titanous salt are commonly used, but both of these solutions are so unstable as to require frequent standardization or elaborate precautions in storage. The use of sodium thiosulfate for the direct titration of a ferric salt has been investigated,' but the conditions under which accurate results can be obtained are apparently very strictly limited.[2] An iodometric method, in which iodide is added to a ferric salt solution and the liberated iodine titrated with thiosulfate, was originally proposed by Mohr.[3]

The iodometric method appeared to offer great advantages, provided a simple process giving exact results could be found. However, experiments

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[1] Kremer, *J. prakt.* **Chem., 84,339 (1861).**

[2] **Norton, Am. J.** *Sci.*, **18,** 25 **(1899).**

[3] **Mohr, Ann.** *Chem. Pharm.*, **105,** 53 **(1858).**

by procedures found in standard texts were unsatisfactory, and statements at variance with these procedures were found in the literature. Thus 'fieadwell-Hall[4] directs that "the greater part of the acid" be neutralized, that five grams of potassium iodide be used, that the air in the flask be removed by carbon dioxide and finally that the reaction be allowed to proceed for twenty minutes. Sutton[5] "nearly neutralizes" the acid, adds "an excess of strong solution of potassium iodide" and heats in a closed flask at 50 60° for about twenty minutes before cooling and titrating. Joseph[6] states that "fair accuracy" can be obtained without taking "any special precautions" if to the ferric solution acidified with hydrochloric acid, "whose amount does not seem to be of any great importance" is added a few grams of potassium iodide and the iodine liberated is titrated "at once." His duplicate analyses show variations as great as 2%. Kolthoff[7] found that accurate results were obtained upon adding 1.5 g. of potassium iodide to 10 ml. of ferric chloride solution which contained 2.5 millimoles of iron and which was 0.1 molal in hydrochloric acid, and then allowing this to stand for five minutes and titrating. The same author also states that more concentrated hydrochloric acid seemed to retard the reaction as well as to cause considerable air oxidation. Kurt Bottger and Wilhelm Bottger[S] carried out a series of experiments in which to 20 ml. of a solution 0.1 molal in sulfuric acid and containing 1.6 millimoles of ferric sulfate they added 10 ml. of a 15% hydrochloric acid solution and allowed this solution to react with 3–4 g. of potassium iodide in a total volume of about 60 ml. for various lengths of time up to one hour. These experiments gave results from 1–2% high. A corresponding series of experiments in which oxygen of the air was eliminated gave correct results. They did not mention the work of Kolthoff. Very recently Grey[g] has studied this method and states: "Numerous experiments have shown that 5.5 moles of potassium iodide are required per atom of iron, and the concentration in the titrated liquid should be adjusted to about $M/7.5$, and the acid concentration should be $N/3$–$3N$. In such a case the liberation of iodine will be strictly proportional to the iron present, within the limits 0.056–56 mg. of iron in 10–50 cc. of liquid." The experimental results are not shown. It is further stated that "the solution after titration by thiosulfate may be shaken violently with air for two hours without any return of the blue color, even when the acidity is that of N hydrochloric acid." This is surprising in view of the observed air

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[4] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1928, Vol. II, 7th ed., p. 577.

[5] Sutton, "Volumetric Analysis," 11th ed., 1924, p. 743.

[6] Joseph, *J. Soc. Chem. Ind.*, 29, 187 (1910).

[7] Kolthoff, *Pharm.* Weekblad., 58, 1510 (1921).

[8] Bottger and Bottger, *Z. anal. Chem.*, 70,214 (1927).

[9] Grey, *J. Chem. Soc.*, 35–39 (1929).

oxidation of iodide in acid solutions which have been reported by others;[10] likewise the possibility that such oxidation may occur previous to the thiosulfate titration is apparently not considered.

Approximate calculations of the equilibrium which should be attained when a ferric salt and iodide react have been made by Bottger and Bottger[8] and by Fales.[11] These calculations indicate that with an excess of iodide, and especially upon reduction of the liberated iodine with thiosulfate, the reaction should be complete within the usual limits of error of volumetric work. Studies of the rate of the reaction between ferric salts and iodide have been made by Schukarew,[12] by Bronsted and Pedersen,[13] by Sasaki,[14] and by Wagner;[15] while the reverse reaction, the oxidation of a ferrous salt by iodine, has been investigated by Banerji and Dhar.[16] Although these investigations were principally concerned with the mechanism of the reactions involved, the results of the rate measurements would seem to indicate difficulty in forcing the reaction to completion within a short time.

In view of this situation, a study of the method was undertaken, especially as to the effect of the acid concentration upon the reaction between the iodide and the ferric salt, as to the amount of "oxygen error" occurring when the titration is carried out in air under various conditions and as to the amount of potassium iodide necessary.[17]

Preparation of the Solutions.—An approximately 0.1 molal solution of ferric chloride was prepared by dissolving an "Analyzed" brand of $FeCl_3 \cdot 6H_2O$ in approximately 0.1 molal hydrochloric acid. Tests for ferrous salt with potassium ferricyanide solution gave negative results. This solution was standardized as to iron content by two different methods. The first three values given below were obtained using the Zimmermann–Reinhardt method; the other values by displacing the chloride in the solution with sulfuric acid, reducing the ferric sulfate with aluminum and titrating the reduced solution with permanganate. An atmosphere of carbon dioxide was maintained during

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[10] (a) Bray and Miller, THIS JOURNAL, 46, 2204 (1924); (b) Popoff and Whitmore, *ibid.*, 47, 2259 (1925); (c) Bottger and Bottger, *Z. anal. Chem.*, 70, 209 (1927).

[11] Fales, "Inorganic Qualitative Analysis," The Century Co., New York, 1925, p. 291.

[12] Schukarew, *Z. physik. Chem.*, 38, 353 (1901).

[13] Bronsted and Pedersen, *ibid.*, 103, 307 (1922).

[14] Sasaki, *Z. anorg. Chem.*, 137, 181–203, 291–327 (1924).

[15] Wagner, *Z. physik. Chem.*, 113, 261 (1924).

[16] Banerji and Dhar, *Z. anorg. allgem. Chem.*, 134, 178 (1924).

[17] A preliminary investigation of this method was made by Mr. Willard A. Findlay. The detailed experimental study was carried out as a group problem by the honor students of a class in quantitative analysis. Experiments numbered 1, 2, 3, 4 and 5 of Table I were performed by S. C. Dorman, R. P. Coleman, R. E. Morris, W. A. Findlay, and J. B. Hatcher, respectively. Experiments 1, 2, 3, 4 and 5 of Table II were carried out by L. E. Kinsler, T. R. White, W. F. Eberz, C. H. Gregory, and G. M. Webb, respectively. The results shown are representative of a larger number of experiments than those actually recorded.

the reduction and titration. The permanganate solution had been standardized against sodium oxalate obtained from the Bureau of Standards. The results of the standardizations of the ferric chloride solution in millimoles per liter were as follows: 99.15, 99.18, 99.15, 98.91, 98.99, 98.91, 99.24, 99.14, 98.95; mean, 99.07.

The sodium thiosulfate solution used was standardized against the same permanganate solution under the conditions recommended by Bray and Miller.[18] Referring the thiosulfate and ferric chloride solutions to the same permanganate solution eliminated the need of knowing the exact absolute value of the permanganate.

Effect of Hydrochloric Acid and of Air.—In order to test the effect of the hydrochloric acid concentration and also the effect of the presence of the oxygen of the air, experiments were carried out as follows: 25-ml. portions of the ferric chloride solution were pipetted into a 250-ml. glass-stoppered conical flask; the amount of hydrochloric acid present was then adjusted to the value shown in the second column of Table I, 3.0 g. of solid potassium iodide was introduced, the solution mixed and the reaction mixture allowed to stand for five minutes in the stoppered flask. The volume of the solution was approximately 30 ml. This solution was then diluted to approximately 100 ml. and immediately titrated with the standard sodium thiosulfate solution, the usual starch indicator being used.

The results are given in Table I. The third column shows the volume of thiosulfate used when this first end-point was obtained. The time

TABLE I

EFFECT OF HYDROCHLORIC ACID IN THE PRESENCE OF AIR

Expt.	Milli-equiv. of HCl present	1st end-point	Ml. of thiosulfate[b] after five minutes	After ten minutes
4	[a]	25.01	25.15	
2	0.25	25.33		
3	0.25	25.30		
5	0.25	25.35		
	Av.	25.33		
1	2.5	25.31	25.32	
1	6.0	25.38		
2	6.0	25.31		
3	6.0	25.34		
4	6.0	25.31	25.32	
5	6.0	25.36		
	Av.	25.34	25.34	
1	12	25.34	25.35	25.36
2	12	25.31		
3	12	25.35		
4	12	25.35		
5	12	25.38		
	Av.	25.35	25.35	25.36
1	24	25.37		
2	24	25.39		
3	24	25.37		
4	24	25.36		
5	24	25.40		
	Av.	25.38		
1	48	25.38	25.39	25.40
2	48	25.36	25.37	
3	48	25.37		
4	48	25.40		25.42
5	48	25.32		25.46
	Av.	25.37	25.37	25.40
1	96	25.52	25.56	
2	96	25.46		
3	96	25.40	25.45	
4	96	25.43		25.45
5	96	25.32	25.44	25.45
	Av.	25.43	25.47	25.47

[a] Neutralized almost to precipitation.

[b] Where volumes and averages are omitted they are the same as in the preceding column.

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[18] Bray and Miller, THIS JOURNAL, 46,2204 (1924).

required for this titration varied from five to ten minutes. To test the stability of this end-point, the solutions were in all cases allowed to stand for two five-minute intervals in the stoppered flask, and if any further iodine color developed it was titrated. The fourth and fifth columns show the total volume of thiosulfate used when more was required. Weight burets or calibrated' volume burets were used in making the titrations. The calculated volume of thiosulfate was 25.33 ml.

In the experiments in which the air was excluded the ferric chloride solution was brought just to boiling for three minutes and then cooled while a rapid stream of carbon dioxide gas was passed above the solution. The potassium iodide was then introduced and the solution allowed to stand for five minutes under a slight pressure, but no appreciable flow, of the carbon dioxide. The solution was then diluted to 100 ml. with water that had been saturated by passing a vigorous stream of carbon dioxide through it and then was titrated. The results of these experiments are shown in Table II. Although the solutions were allowed to stand for two five-minute intervals after obtaining the first end-point, in no case did further iodine color develop after the first five-minute interval. The calculated volume of thiosulfate was 25.33.

TABLE II

EFFECT OF HYDROCHLORIC ACID IN THE PRESENCE OF CARBON DIOXIDE

Expt.	Milli-equiv. of HCl present	1st end-point	Ml. of thiosulfate[b] after five minutes	Expt.	Milli-equiv. of HCl present	1st end-point	Ml. of thiosulfate[b] after five minutes
1	[a]	25.03		1	24	25.33	
2		25.18	25.21	2	24	25.10	25.29
3		25.29		3	24	25.37	
4		24.55	24.74	4	24	25.29	25.34
5		25.25		5	24	25.26	25.33
	Av.	25.06	25.10		Av.	25.27	25.33
1	6	25.39		1	48	25.32	
2	6	25.21	25.22	2	48	25.19	25.30
3	6	25.26		3	48	25.34	
4	6	25.34		4	48	25.31	25.35
5	6	25 31		5	48	25.27	25.34
	Av.	25.30	25.30		Av.	25.28	25.33
1	12	25.39		1	96	25.30	25.32
2	12	25.25	25.38	2	96	25.15	25.29
3	12	25.37		3	96	25.30	25.34
4	12	25.35		4	96	25.28	25.34
5	12	25.33		5	96	25.27	25.33
	Av.	25.34	25.36		Av.	25.26	25.32

[a] Neutralized almost to precipitation.

[b] Where volumes and averages are omitted they are the same as in the preceding column.

Effect of the Iodide Concentration.—To determine the effect of varying the potassium iodide used, experiments were carried out by Mr. Willard A. Findlay in air and with conditions similar to those in Table I, using 12 milli-equivalents of hydrochloric acid and the amount of potassium iodide indicated in the first column of Table III. The calculated volume of thiosulfate was 34.68 ml.

TABLE III

EFFECT OF EXCESS OF IODIDE WHEN USING HYDROCHLORIC ACID

KI used, g.	1st end-point	Ml. of thiosulfate after five minutes	After ten minutes
1.0	33.95	34.22	34.40
2.0	34.5	34.58	34.58
3.0	34.67	34.67	34.67
5.0	34.67	34.67	34.67

Effect of the Presence of Sulfuric Acid and of the Iodide Concentration.—A brief study was made by Mr. W. A. Findlay of the reaction between iodide and ferric sulfate in sulfuric acid solution. An approximately 0.1 molal ferric sulfate solution which was 0.25 molal in sulfuric acid was used. The procedure was the same as with the hydrochloric acid solutions in the presence of air with the exception that 4 g. of potassium iodide was added. The effect of the amount of sulfuric acid present is shown in Table IV. The calculated volume of thiosulfate was 29.31 ml.

TABLE IV

EFFECT OF SULFURIC ACID IN THE PRESENCE OF AIR

H_2SO_4 present, milli-equivalents	1st end-point	Ml of thiosulfate after five minutes	After ten minutes
Neutralized	27.35	27.72	27.77
6	29.12	29.19	29.25
12	29.29	29.34	29.37
18	29.28	29.29	29.29
18	29.32	29.34	29.34
18	29.27	29.30	29.32
24	29.37	29.37	29.39
30	29.39	29.39	29.42
72	29.49	29.49	29.51

The experiments shown in Table V were made to show the effect of the excess of iodide present when using sulfuric acid. The procedure was the

TABLE V

EFFECT OF EXCESS OF IODIDE WHEN USING SULFURIC ACID

KI used, g.	1st end-point	Ml. of thiosulfate after five minutes	After ten minutes
0.5	13	14	15
1.0	22.6	23.5	24.0
2.0	28.80	28.92	29.30
3.0	29.18	29.26	29.26
4.0	29.28	29.29	29.29
8.0	29.36	29.36	29.37

same as that above, 18 milli-equivalents of sulfuric acid being present. The calculated volume of thiosulfate was 29.31 ml.

Discussion of the Results

The experiments given in Table I, which were carried out in the presence of air, show that under the conditions of the procedure used permanent end-points and results consistent to 0.2% can be obtained when there are present 0.25 to 12 milli-equivalents of hydrochloric acid in 30 ml. of solution. If the solution is nearly neutralized unstable end-points and low results are obtained. This is to be expected because of the hydrolysis of the ferric chloride under these conditions. With more than 24 milli-equivalents of hydrochloric acid the "oxygen error" becomes pronounced, as shown by the unstable end-points and high results. The experiments given in Table II, carried out under carbon dioxide, show that the accuracy obtained in the presence of air when less than 12 milli-equivalents of acid was present is at least partly due to compensating errors, namely, to a negative error, probably caused by insufficient acid to prevent hydrolysis of the ferric chloride, and a positive "oxygen error." When 12 milli-equivalents of hydrochloric acid are present during this reaction between iodide and ferric chloride, or the acid is approximately 0.5 mold, the values obtained in carbon dioxide reach a maximum. The decrease observed in the values for the first end-point as the acid is increased above 12 milli-equivalents, while possibly a rate effect, is in accord with the decrease in the potential of the ferric-ferrous electrode which has been observed by Carter and Clews[19] and by Popoff and Kunz,[20] as the hydrochloric acid in the solution is increased. This effect is attributed by these authors to complex formation between the hydrochloric acid and the ferric chloride. When air is present this effect is overcome by a greater oxygen error. It is indicated that the oxygen error is at a minimum when the hydrochloric acid concentration is most favorable for the reaction between the ferric chloride and iodide. The experiments given in Table III show that 3 g. of potassium iodide is the minimum amount permissible under the conditions of these experiments. The experiments of Tables IV and V indicate that the effect of sulfuric acid is to increase the amount of acid and of iodide necessary and to make the end-point less stable. The above results are confirmatory of the experiments and conclusions of Kolthoff.

Test Analyses

In order to test this method the following analyses were carried out by Mr. C. H. Gregory. A sample containing 2.3667 g. of "Sibley" Iron Ore, Standard Sample No. 27 of the Bureau of Standards and containing ac-

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[19] Carter and Clews, J. Chem. *Soc.*, **125, 1880** (1924).

[20] Popoff and Kunz, THIS JOURNAL, **51, 382** (1929).

cording to the average of the Bureau of standards determinations 69.26% iron, was weighed out. This was treated with hydrochloric acid and the insoluble residue was filtered out and treated with hydrofluoric acid in a platinum crucible; the hydrofluoric acid was expelled by adding sulfuric acid and evaporating this just to dryness. The residue remaining was dissolved in hydrochloric acid and added to the first solution. Dilute permanganate solution was added to this cold solution until the first perceptible pink color was noted and the solution then evaporated until the volume was about 5 ml. Five ml. of 6 molal hydrochloric acid was then added, the solution diluted to 250 ml. in a weighed flask and the flask and solution weighed. Two approximately 25-ml. portions of this solution were then weighed into conical flasks and treated by the same procedure as was used in obtaining the results shown in Table I. Two other samples were then treated by the same procedure, except that the air was displaced by carbon dioxide in the manner previously described. Weight burets were used in the titrations. The results of these analyses are shown in Table VI.

TABLE VI

ANALYSIS OF IRON ORE NO. 27 OF THE BUREAU OF STANDARDS

Method	Air not removed	Air not removed	Under CO_2	Under CO_2
Fe found, %	69.23	69.19	69.16	69.16
Fe present, %	69.26	69.26	69.26	69.26

Summary

The conditions determining the reliability of the simple iodometric determination of ferric iron originally suggested by Mohr have been studied. Experiments have been described which show that an accuracy of 0.2% is obtained when the reaction between the ferric chloride and iodide is allowed to take place in a closed flask for five minutes in about 30 ml. of a solution which contains 3 g. of potassium iodide and from 0.25 to 25 milli-equivalents of hydrochloric acid, and this solution is then diluted to approximately 100 ml. and titrated with thiosulfate. Permanent end-points are obtained under these conditions. The accuracy of this procedure has also been confirmed by test analyses.

Experiments carried out under carbon dioxide show that this accuracy is in most cases partly the result of compensating errors—an incomplete reaction and an "oxygen error."

When sulfuric acid is used more acid is required, a higher concentration of iodide is necessary and the end-points are not as permanent.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO BORON'. I. REACTION OF BORON TRIFLUORIDE WITH AMMONIA AND ALKYLAMINES

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I. Introduction

The chemistry of boron is of particular interest in the light of the modern atomic theory. Seemingly, boron has a marked tendency to form compounds corresponding to a valence greater than might be expected from its position in the periodic system. This is best seen in the simplest hydride whose composition corresponds to the formula BH_3 but whose molecular weight corresponds to the formula B_2H_6.[1] The tendency of boron to function with a higher valence than **3** also appears in other compounds. Thus Krause,[2] in reducing triphenylboron with the alkali metals in ether, obtained a salt corresponding to the formula $NaB(C_6H_5)_3$. The electron due to sodium is evidently associated with the triphenylboron group, but it is not held very firmly since it is reduced by triphenylmethyl. Triphenylboron also forms remarkably stable compounds with one molecule of ammonia or an amine.[3] When these compounds are reduced by means of the alkali metals in suitable solvents,[4] they add an atom of metal to form compounds of the type $NaB(C_6H_5)_3{\cdot}NH_3$. Trimethylboron also combines with various hydroxides[5] and triphenylboron combines with the amides[6] of the alkali metals. These compounds are now under investigation and will be reported later.

The boron trihalides appear to have a marked tendency to combine with ammonia or amines. In particular, boron trifluoride combines with ammonia with the evolution of a great deal of heat to form a seemingly stable solid compound. Unfortunately, it is not easy to distinguish between an addition compound and a mixture of compounds due to ammonolysis. It is the purpose of the present investigation to determine definitely whether or not boron trifluoride is capable of adding ammonia or an amine directly without ammonolysis. As the results will show, this is the case, although, at the same time, there is clear evidence that, when boron trifluoride is dissolved in ammonia or an amine, it is ammonolyzed to an appreciable extent.

The reaction between boron trifluoride and ammonia was first observed

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[1] Stock and Friederici, *Ber.*, **46, 1959 (1913).**

[2] Krause and Polack, *ibid.*, **59,** 777 **(1926).**

[3] Stock and Zeidler, *ibid.*, **54, 531 (1921);** Krause, **ibid., 57,813 (1924).**

[4] Unpublished observations by Wade B. Robinson in this Laboratory.

[5] Frankland, **Ann. *Chem.*,** 124, **129 (1862).**

[6] Unpublished observations by W. W. Hawes in this Laboratory,

by Gay-Lussac.[7] The reaction was further studied by J. Davy.[8] Neither of these investigators definitely established whether or not an addition compound is formed. Davy, in particular, showed that the initial solid compound is soluble in excess of ammonia.

According to Mellor,[9] the solid compound is probably monoammino-boron trifluoride, $BF_3 \cdot NH_3$, while the products containing greater quantities of ammonia are mixtures of ammonium fluoride and boron amides.

Mixter[10] prepared monoammino boron trifluoride by passing boron trifluoride into dry ammonia gas. He analyzed this product for ammonia and found values approximating that required for the formula $BF_3 \cdot NH_3$. He determined the molecular weight of the vapor of this material by the Victor Meyer method at temperatures above the melting point of zinc. The values found lay in the neighborhood of 46, or approximately one-half that of monoammino boron trifluoride, indicating practically complete dissociation of the compound into its constituents.

Joannis[11] studied the interaction between boron trichloride and liquid ammonia and concluded that the chloride is completely ammonolyzed. This might lead one to infer that a similar reaction occurs in the case of boron trifluoride. It should be noted, in this connection, that the weight of the final product gives no safe indication of whether or not ammonolysis has occurred. Thus, reaction might take place as follows

$$2\ BF3 + 2\ NH3 = NH_4BF_4 + BF_2NH_2$$

If boron trifluoride ammonolyzes with the formation of ammonium fluoride, the latter compound might well combine with boron trifluoride to form ammonium borofluoride. The resulting mixture would have the same composition as a compound of the formula $BF_3 \cdot NH_3$.

As indicating a marked tendency of boron trifluoride to form addition compounds, it might be mentioned that Gasselin[12] found that it combines readily with one molecule of ether to form a comparatively stable product boiling at 125°. An ether solution of boron trifluoride was found very useful in the present investigation in preparing pure compounds of boron trifluoride with ammonia and various amines.

II. Preparation and Properties of Monoammino Boron Trifluoride

Materials.—Boron trifluoride was prepared by heating a mixture of ammonium borofluoride with a slight excess of boric oxide in concentrated sulfuric acid.

Ammonium borofluoride was prepared by dissolving boric acid in a slight excess

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[7] Gay-Lussac, *Mémoires de la Société d'Arcueil*, **2,** 211 (1809).

[8] *J.* Davy, *Phil. Trans.*, **30,** **365** (1812).

[9] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1924, Vol. V, p. 122.

[10] W. G. Mixter, *Am. Chem. J.*, **2,** 153 (1881).

[11] Joannis, *Compt. rend.*, **135,** 1106 (1902).

[12] Gasselin, *Ann. Chim.*, **3,** 50 (1894).

of aqueous hydrogen fluoride and neutralizing with ammonium hydroxide. The solution was concentrated, filtered and allowed to cool, when fine colorless crystals separated.

Preparation of $BF_3 \cdot NH_3$.—A reliable method for the preparation of monoammino boron trifluoride was not found in the literature. Accordingly, four different methods were tried out, of which the last proved the most convenient. These methods were: (1) to pass a mixture of dry nitrogen and boron trifluoride through liquid ammonia, (2) to introduce alternately small quantities of boron trifluoride and ammonia into an evacuated bulb at room temperatures, (3) to bubble pure boron trifluoride into liquid ammonia from underneath a surface of mercury, (4) to saturate an ether solution of boron trifluoride with ammonia.

Methods 1 and 2 were quite unsatisfactory. Method 3 proved fairly convenient but the presence of mercury was disadvantageous. Method 4 proved satisfactory and may be described in some detail. The desired quantity of boron trifluoride, dissolved in ether, is saturated with ammonia at zero degrees by passing a stream of ammonia vapor over the surface of the solution under constant agitation. Monoammino boron trifluoride is precipitated as a fine, white solid. The supernatant liquid is decanted and adhering solvent removed by means of a pump.

Properties of $BF_3 \cdot NH_3$.—Monoammino boron trifluoride is soluble in liquid ammonia, ethylamine and diethylamine. It is practically insoluble in ether, benzene and petroleum ether. When heated in an evacuated tube, it sublimes at temperatures above 180°, leaving only a slight residue. Fusion sets in at 180°, an opaque pasty mass resulting. This seems to indicate that under these conditions the material is not homogeneous.

Monoammino boron trifluoride, dissolved in liquid ammonia, is appreciably ammonolyzed, since, when treated with metallic sodium, hydrogen is evolved. The reaction takes place in several stages, indicating that not all the fluorine atoms are hydrolyzed with equal ease. The fact that the corresponding ethylamine derivative can be completely ammonolyzed by means of lithium in ethylamine leaves no doubt that an analogous reaction occurs in liquid ammonia.

Analysis of Monoammino Boron Trifluoride.—The compound prepared by passing ammonia through an ethereal solution of boron trifluoride was analyzed for ammonia and boron. To determine the ammonia, an alkaline solution of the compound was distilled, the distillate being collected in an excess of 0.1 N hydrochloric acid which was titrated back with 0.1 N sodium hydroxide.

Anal. Subs., 0.3151, 0.4147: 36.33, 48.01 cc. of 0.1021 N HCl. Calcd. for $BF_3 \cdot NH_3$: N, 16.47. Found: N, 16.48, 16.54.

In analyzing for boron, weighed samples were dissolved in water containing a slight excess of sodium hydroxide. The resulting solutions were neutralized with 0.1 *N* hydrochloric acid, using methyl red as indicator. When the end-point was reached, about 1 g. of mannitol was added and the boric acid titrated with 0.1 N sodium hydroxide, using phenolphthalein as indicator.

Anal. Subs., 0.1829, 0.2949, 0.5671: 21.98, 31.66, 62.65 cc. of 0.10727 *N* NaOH. Calcd. for $BF_3 \cdot NH_3$: B, 12.95. Found: B, 14.25, 12.65, 13.00.

The nitrogen content of the compound is in good agreement with the formula $BF_3 \cdot NH_3$ but the boron analyses are less satisfactory. In fact, unless conditions can be carefully controlled, it is extremely difficult to get entirely satisfactory results for boron by any of the usual analytical methods.

As will be shown below, boron trifluoride combines with triethylamine to form the compound $BF_3 \cdot N(C_2H_5)_3$. When this compound is treated with ammonia, a product is formed which has the properties of monoammino boron trifluoride. Its solubility, melting point and other properties correspond closely with those of the compound directly precipitated by passing ammonia into an ethereal solution of boron trifluoride. The product formed by the treatment of the triethylamine derivative with ammonia was analyzed for nitrogen, as described above.

Anal. ($BF_3 \cdot NH_3$ precipitated from triethylamine). Subs., 0 0394, 0.0275: 4.54, 3.19 cc. of 0.1021 *N* HCl. Calcd. for $BF_3 \cdot NH_3$: N, 16.47. Found: N, 16.46, 16.52.

It was found that monoammino boron trifluoride is soluble in triethylamine in the presence of excess ammonia. When the excess ammonia is slowly removed, the ammonia derivative crystallizes from the solution. A quantity of this material was prepared and analyzed for nitrogen.

Anal. (Recrystallized $BF_3 \cdot NH_3$). Subs., 0.1192, 0.0947: 13.88, 11.01 cc. of 0.1021 N HCl. Calcd. for $BF_3 \cdot NH_3$: N, 16.47. Found: N, 16.63, 16 61.

The analyses show that the product formed on passing ammonia through an ethereal solution of boron trifluoride has a mean composition corresponding to the formula $BF_2 \cdot NH_3$. Either a compound corresponding to this formula exists or the product consists of a mixture of BF_2NH_2 and NH_4BF_4. Since the compound prepared by the action of ammonia on a triethylamine solution of boron trifluoride is identical with that obtained from an ethereal solution and since, moreover, the product formed in ethylamine is completely soluble in this solvent in the presence of excess ammonia and can be recrystallized from this solvent, and since, further, the crystallized product, on analysis, shows a composition corresponding to the formula $BF_3 \cdot NH_3$, it follows that the original product formed by the action of ammonia on the ethereal solution of boron trifluoride is, in fact, an addition compound $BF_3 \cdot NH_3$. Triethylamine is a very indifferent solvent for salt-like substances, being inferior even to ether in this respect. It is inconceivable that ammonium borofluoride would be soluble in such a mixture. Furthermore, in the process of recrystallization, there is no evidence of a second product. Accordingly, it may be concluded that boron trifluoride combines with one molecule of ammonia to form the compound $BF_3 \cdot NH_3$.

III. Triethylammino Boron Trifluoride

Preparation.—The interaction between boron trifluoride and triethylamine is of particular interest since ammonolysis cannot well take place in this solvent. The compound was first prepared by introducing a known quantity of triethylamine into a weighed reaction tube cooled to liquid ammonia temperatures, into which an excess of boron trifluoride was then introduced. When the reaction was completed, the excess fluoride was pumped off and the reaction tube was weighed. Thus the amount of boron trifluoride combined with the amine could be found.

The product formed was a solid melting at room temperatures and turning brown upon standing for a comparatively short time. In three experiments the following results were obtained: 3.125, 0.534, 1.565 g. of amine combined with 1.924, 0.392, 0.928 g. of BF_3. These data yield for the ratio $BF_3/(C_2H_5)_3N$ the values 0.951, 1.076, 0.877.

In other words, approximately 1 mole of boron trifluoride was found to combine with one mole of triethylamine. It was found that the product is soluble in the presence of excess ammonia and that it is reprecipitated in crystalline form as the ammonia is removed. The resulting crystalline material appeared to be identical with monoammino boron trifluoride.

In one experiment ammonia was added to the triethylamine derivative, after which the tube containing the material was pumped to constant weight at $-33°$. Under these conditions the excess ammonia, as well as the triethylamine formed in the reaction with ammonia, was removed. It was found that 2.4821 g. or 0.0246 mole of amine initially combined with 1.6805 or 0.0247 mole of BF_3 and, after treating with ammonia, the weight indicated the presence of 0.4389 g. or 0.0258 mole of NH_3. From these data it is seen that 1 mole of boron trifluoride combines with 1 mole of triethylamine which, in turn, may be substituted quantitatively by ammonia. The final product obtained in this reaction was analyzed for ammonia, the data being given on page 2693.

A second and more satisfactory method of preparing triethylammino boron trifluoride consists in treating an ethereal solution of the trifluoride with an excess of triethylamine at liquid ammonia temperatures. The amine (in excess) was condensed on the ethereal solution of BF_3 and when the two layers were mixed, a white precipitate was formed. This precipitate melted at room temperatures and rapidly acquired a brown tint, indicating some decomposition. After removing all excess materials, the product was finally distilled at a temperature of 80° under a pressure of 3 mm. The liquid which distilled over solidified in the colder portions of the apparatus. This compound proved to be triethylammino boron trifluoride $(C_2H_5)_3N{\cdot}BF_3$.

Analysis and Molecular Weight.—The nitrogen content of the redistilled material was determined by adding water and boiling off the amine in an evacuated two-legged tube. The distillate was titrated with standard hydrochloric acid.

Anal. Subs., 0.0783, 0.0688: 5.13, 4.41 cc. of 0.09077 *N* HCl. Calcd. for $(C_2H_5)_3N{\cdot}BF_3$: N, 8.27. Found: N, 8.32, 8.14.

The fluorine content of the compound was determined as lead chlorofluoride. The sample was dissolved in water and 16 drops of concentrated hydrochloric acid were added, after which the solution was made slightly acid with nitric acid and 10 drops of acetic acid were added. Lead chlorofluoride was precipitated on the addition of a 10% solution of lead acetate.

Anal. Subs., 0.0389, 0.0889: PbClF, 0.1751, 0.4068. Calcd. for $BF_3{\cdot}(C_2H_5)_3N$: F, 33.69. Found: F, 32.67, 34.38.

The analyses for fluorine are not entirely satisfactory but, as is well known, it is extremely difficult to obtain satisfactory analyses for this element, particularly with the small quantities of material available. There can be no doubt, however, that the compound involves a single molecule each of triethylamine and boron trifluoride. This was further borne out by its molecular weight in benzene as determined by the freezing-point method.

Molecular weight of $BF_3{\cdot}(C_2H_5)_3N$ in benzene: solute, 0.1262, 0.2312, 0.3574 g.; solvent, 22.69, 22.69 g.; *At,* 0.170°, 0.300°, 0.437°; mol. wt. found, 163.5, 169.8, 180.1; mol. wt. calcd. for $(C_2H_5)_3N{\cdot}BF_3$, 169.2.

As may be seen from the data given, the molecular weight of the compound in benzene solution corresponds closely to that required.

Properties.—Triethylammino boron trifluoride melts sharply at 29.5°. It decomposes slowly, especially at room temperatures, turning brown and giving off amine. It is very soluble in alcohol, benzene, ether and hot petroleum ether. It is difficultly soluble in water, but if first dissolved in a small quantity of ether the resulting solution is completely soluble in water. The compound, when dissolved in triethylamine, is not affected by freshly cut sodium or lithium.

IV. Diethylammino Boron Trifluoride

Preparation.—Monoammino boron trifluoride was dissolved in diethylamine, the excess amine removed with a pump, the product washed with ether and the last traces of solvent were removed with a pump. The product was a white solid which melted at 150–151°.

Anal. Subs., 0.0672, 0.0817: 5.31, 5.96 cc. of 0.09077 N HCl. Calcd. for $BF_3\cdot(C_2H_5)_2NH$: N, 9.91. Found: N, 10.41, 8.27.

In one experiment 0.9648 g. (0.0113 mole) of $BF_3\cdot NH_3$ was treated with diethylamine in a weighed reaction tube. After exhausting, the product weighed 1.6054 g. Assuming that the ammonia was replaced by diethylamine, the weight of amine present corresponded to 0.0118 mole, which agrees fairly well with 0.0113, the number of moles of boron trifluoride present.

In another preparation diethylamine was distilled into an ethereal solution of boron trifluoride at liquid ammonia temperatures. A white crystalline solid was formed, the supernatant liquid was decanted and the solid was washed several times with ether. It was then dried rapidly on a filter paper. It melted at 165° but not sharply.

Anal. Subs., 0.1360, 0.1113: 9.34, 9.69 cc. of 0.09077 N HCl. Calcd. for $BF_3\cdot(C_2H_5)_2NH$: N, 9.91. Found: N, 8.72, 8.79.

On analyzing this material for boron by the lead chlorofluoride method, there were obtained, respectively, 46.33 and 45.00% of fluorine against 40.36 required.

In another preparation an ethereal solution of boron trifluoride was added drop by drop to diethylamine cooled in ice water. The resulting product was dissolved in alcohol and ether was added to precipitate the compound. After washing, the product was dried on a pump and analyzed.

Anal. Subs., 0.0613, 0.0812: 3.73, 4.84 cc. of 0.1083 N HCl. Calcd.: N, 9.91. Found: N, 9.23, 9.04.

Several analyses for fluorine yielded 50% in place of 40.36% required for the compound $BF_3\cdot(C_2H_5)_2NH$. None of the analyses, either for fluorine or nitrogen, is entirely satisfactory. The first preparation gave, on the whole, the most satisfactory results. Seemingly the compound loses diethylamine fairly readily. This is further borne out by the fact that the melting points obtained were variable and in general not sharp.

Properties.—Diethylammino boron trifluoride is practically insoluble in ether, benzene and petroleum ether. It is very soluble in diethylamine, alcohol and water. It melts in the neighborhood of 160°. The high melting point is quite unexpected as the triethylamine derivative melts at 29.5° while the ethylamine derivative melts at 89°.

V. Ethylammino Boron Trifluoride

Preparation.—The ethylamine derivative was prepared by condensing a quantity of ethylamine on monoammino boron trifluoride in one leg of a two-legged tube. Any undissolved material was allowed to settle out, after which the supernatant liquid was decanted into the second leg of the tube. The excess of amine was then distilled and the last traces were removed by means of a pump.

The compound was also prepared by adding an excess of amine to an ethereal solution of boron trifluoride and distilling off the ether and excess amine.

Analyses.—Products prepared as described above were analyzed for nitrogen in the usual manner.

Subs., **0.0736, 0.0756, 0.2250, 0.2315: 6.40, 7.31, 19.51, 20.16** cc. of **0.1021** *N* HCl. Calcd. for $BF_3\cdot(C_2H_5)NH_2$: N, 12.38. Found: N, **12.43, 13.82, 12.39,** 12.45.

The product was likewise analyzed for fluorine by the lead chlorofluoride method.

Subs., **0.0782, 0.0920:** PbClF, **0.559, 0.6851.** Calcd. for $BF_3\cdot(C_2H_5)NH_2$: F, **50.39.** Found: F, **51.60, 51.94.**

The molecular weight of the ethylamine derivative was determined in ether by a modification of the Cottrell method.

Subs., **0.3253, 0.1505, 0.0704;** ether, 33.06, **29.23, 40.37;** *At,* 0.141°, 0.1079°, **0.029'.** Calcd. for $BF_3\cdot(C_2H_5)NH_2$: mol. wt., **113.1.** Found: mol. wt., **147.0, 137.5, 133.3.**

Properties.—Ethylammino boron trifluoride melts sharply at 89°. It decomposes rapidly when heated in air above its melting point. It is soluble in benzene and slightly soluble in ether, from which solvents it may be recrystallized. Its reaction with lithium in ethylamine solution will be described in a subsequent paper.

Taking into account the results of analysis and molecular weight determinations, as well as the fact that the compound may be recrystallized from various solvents, there can be little doubt that ethylamine forms an addition compound with boron trifluoride corresponding to the formula $BF_3\cdot(C_2H_5)NH_2$.

Summary

1. Several methods for the preparation of monoammino boron trifluoride, $BF_3\cdot NH_3$, are described. This compound has been characterized and some of its properties determined.

2. Boron trifluoride combines with triethylamine to form the compound $BF_3\cdot(C_2H_5)_3N$, which melts at 29.5°. The method of its preparation and its properties are described.

3. Boron trifluoride combines with diethylamine to form the compound $BF_3\cdot(C_2H_5)_2NH$, which melts in the neighborhood of 160°. This compound is relatively less stable than other ammino derivatives and has not been so well characterized.

4. Boron trifluoride combines with ethylamine to form the compound $BF_3\cdot C_2H_5NH_2$, which melts at 89°. The properties of this compound are described and methods of preparation are given.

PROVIDENCE, RHODE ISLAND

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

THE DECOMPOSITION OF THALLIC OXIDE[1]

BY A. B. F. DUNCAN

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In studies of the thermal decomposition of metallic oxides, relatively little attention has been paid to the influence of particle size on the equilibrium oxygen pressures. L. Wöhler,[2] in a study of the decomposition of several oxides, observed that the equilibrium pressure of a sample at a fixed temperature was not constant but gradually fell. A. J. Allmand[3] attributed this to changes in particle size during heating, while Wohler claimed that solid solutions of the products with the original oxide were formed. The influence of particle size on the decomposition of carbonates and mercuric oxide has been studied by Centnerszwer and co-workers[4]

If a sample of oxide is prepared by precipitation in cold solution, or from a hydroxide by dehydration at low temperatures, the sample would usually contain a large proportion of very small particles. If the oxide loses oxygen at low temperatures, at which there is a slow rate of growth of the particles to larger ones, we may obtain apparent equilibrium values which are in error due to the fact that the original solid was not in a thermodynamic steady state. By varying the conditions of precipitation and dehydration we get samples which give different equilibrium pressures at the same temperature. If a quantity of oxygen is withdrawn after the equilibrium pressure is reached and a lower equilibrium pressure is obtained at the same temperature, it cannot be decided whether a solution has been formed or whether a change in the degree of dispersion of the solid has taken place.

Matters are somewhat simplified when we can work with oxides above their melting points. The size of the particles no longer enters the question and any lowering of the decomposition pressure must show solution. Milan has recently studied[5] the decomposition of vanadium pentoxide above its melting point and found that small quantities of the lower oxide, V_2O_4, lowered the decomposition pressure of pure V_2O_5 by large amounts.

Experiments on the loss of oxygen by thallic oxide have been made by Lamy,[6] T. Carnelley and J. Walker,[7] and O. Rabe.[8] The behavior of this

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[1] From the dissertation submitted by A. B. F. Duncan in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Wöhler, Z. *Elektrochem.*, 17, 98 (1911).

[3] Allmand, J. *Chem. Soc.*, 97, 618 (1910).

[4] Centnerszwer and co-workers, Z. *physik. Chem.*, *124*, 225 (1926); 130, 189 (1927); 132, 185 (1928).

[5] Milan, J. *Phys. Chem.*, 33, 498 (1929).

[6] Lamy, Ann. *Chem. Phys.*, [3] *67*, *400* (1863).

[7] Carnelley and Walker, J. *Chem. Soc.*, *53*, (1888).

[8] Rabe, *Z. anorg. Chem.*, 55, 136 (1907).

oxide on being heated seems to depend on its method of preparation. If the oxide is prepared from the hydrate, $Tl_2O_3 \cdot H_2O$, it loses oxygen below 100°, before all the water is removed. The brown crystalline modification loses oxygen below 500°, but according to Rabe[9] the black crystalline modification may be heated for hours at 500° without change. The behavior of Tl_2O_3 heated in a vacuum has not been studied. The decomposition of the oxide is thus seen to depend on the method of preparation, but the brown forms change over to the black by melting under a pressure of oxygen sufficient to prevent decomposition.

Two experimental difficulties are met in the study of the decomposition of thallic oxide. The oxides are chemically active and attack fused quartz, forming silicates, and dissolve platinum and silver. In addition, thallous oxide is somewhat volatile at the temperatures used and would distil into cooler parts of the apparatus, changing the composition of the residue, or react with the fused quartz, leaving an excess of oxygen. In this work a vessel of pure fused magnesium oxide[10] was found to be satisfactory since it was not attacked chemically and apparently not dissolved by the oxides. The pure oxide was molded, sintered at a high temperature and finally heated at 2500° in the induction furnace. The surface was well glazed. The second difficulty was avoided by enclosing the crucible and oxide in a vacuum-tight vessel of pure silver. At high temperatures oxygen quickly diffused through the walls but the thallous oxide could not, so it was all kept at constant temperature. Details in regard to the construction of this vessel are given in the following section.

Apparatus

The apparatus consisted of the fused quartz reaction tube, a water jacketed gas buret, a manometer, a McLeod gage and a mercury vapor pump backed by an oil pump. The pumps could be cut off from the apparatus by a mercury trap.

The manometer was a U-tube, both arms being one meter long. The top of one arm was connected to the reaction tube and gas buret and the other arm led to the McLeod gage and pumps. At the bottom of the U was sealed a tube 80 cm. long, carrying rubber hose and leveling bulb. With the mercury bulb lowered the manometer, reaction vessel and gas buret could be put in connection with the pumps and McLeod gage. By raising the mercury the manometer gave direct pressure readings provided a high vacuum was maintained over the arm connected to the pumps. The manometer and scale to which it was fixed was calibrated. The fused quartz reaction tube is shown in Fig. 1. The platinum–platinum-10% rhodium thermocouple was in the inner fused quartz tube and the hot junction about three millimeters from the silver cup, well in the zone of constant temperature of the furnace. Temperatures were measured on a Leeds and Northrup portable potentiometer, and are considered accurate to 3°. The platinum furnace has been described.[11] The gas buret and fused quartz tube were connected to

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[9] Rabe, *Z. anorg. Chem.*, **48**, 431 (1906).

[10] We are indebted to the Bureau of Standards, Pyrometer Division, for their cooperation in making this vessel.

[11] Morse and Frazer, *Am. Chem. J.*, **32**, 93 (1904).

the manometer by graded seals. The volume was made as small as possible by the use of capillary pyrex tubing. The space within the quartz–pyrex graded seal was taken by a closely fitting glass tube sealed at both ends.

The silver cup was designed so that it could be filled with oxygen at atmospheric pressure and sealed in that condition. The silver was specially purified in this Laboratory. The bottom cylindrical cup was 5 cm. high, 2.5 cm. in diameter, 0.17 mm. thick and was spun in one piece. The top, also spun in one piece, had a rim projecting upward 1.5 cm., and fitted closely in the cup. In the center of the top was a cone which had a small hole in the tip.

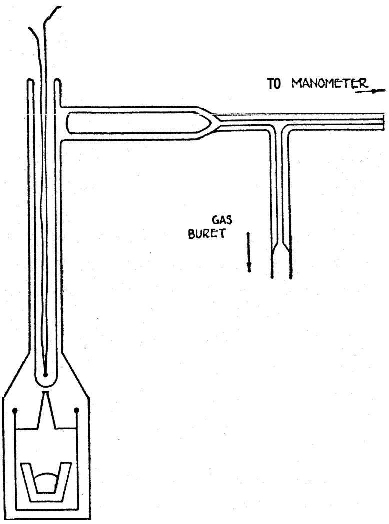

Fig. 1.

Sealing the Silver Cup.—A weighed sample of thallic oxide was placed in the magnesia crucible which was placed in the silver cup. The top was put in place and fused to the cup with a small oxygen–gas flame, without the use of solder. During this operation, the cup was partly immersed in water.

After sealing, the cup was placed in the pyrex tube shown in Fig. 2, which was sealed to the manometer and gas buret. Then with the lower stopcock closed and the upper opened the apparatus, including the interior of the silver cup, was thoroughly pumped out. Then the volume of the apparatus was found by admitting a known quantity of air and measuring the pressure. The air was pumped out and oxygen (99.8%) was admitted to atmospheric pressure. Then a rapid stream of oxygen was started from a tank through a rubber tube. The upper stopcock was closed. The rubber tube was fitted on the lower stopcock, which was quickly opened and the ground joint disconnected. With oxygen rapidly passing upward around the cup the hole was closed as tightly as possible by pressing the tip of the cone with pliers. Then the cup was taken out and the tip sealed by melting in the oxygen–gas flame. The cup was replaced in the pyrex tube, the apparatus pumped out and the volume of the apparatus again determined. The volume was shown to be much less and the decrease in volume minus the volumes of silver, magnesia and thallic oxide gave the oxygen inclosed.

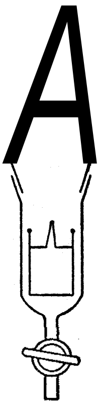

Fig. 2.

Preparation of Thallic Oxide.—The method of preparing black crystalline thallic oxide given by Rabe[8] was used with slight modification. The product was washed with 5 N nitric acid, then with hot water until free from acid and dried at 120". It was later fused under an oxygen pressure greater than the decomposition pressure. The product used consisted of well-defined black needles.

Experimental Procedure

The silver cup after sealing was sealed inside the fused quartz container shown in Fig. 1. This was packed in the furnace and then sealed to the apparatus. The total volume of the reaction system was found by admitting a known quantity of air and reading pressure after the mercury had been raised above the gas buret to a mark on the capillary tubing.

The reaction tube was evacuated for several days with the furnace heated to 450°. The furnace was brought to 750° and oxygen admitted from the gas buret to 760 millimeters' pressure. After heating at this temperature and pressure for several hours, the furnace was slowly cooled, the oxygen pressure being kept constant at 760 millimeters. The system was pumped out. The mercury was raised above the stopcock of the gas buret and the manometer set; then the following experiments were made.

The oxygen pressures at five different temperatures were measured. To insure equilibrium the temperature was kept constant until there was no further change in pressure. The temperature was increased for a time and then changed to its former value, at which the pressure also assumed its former value. Pressures were measured to the nearest millimeter. After cooling very slowly to room temperature the pressure remaining was less than one millimeter.

The furnace was heated and the mercury drawn back into the gas buret. When a sufficient quantity of oxygen had collected, a definite volume at known temperature and pressure was withdrawn from the system by closing the stopcock of the buret. The mercury was raised above the stopcock and the furnace slowly cooled. The melt contained a mixture of thallic and thallous oxides and the composition was fixed by the oxygen removed.

The oxide mixture was heated at the same temperatures that were used previously and measurements of the equilibrium pressures were obtained. At the conclusion another definite quantity of oxygen was removed. Four series of pressure measurements were made, representing the decomposition of the pure oxide and three different mixtures of the two oxides.

During the fifth series of measurements erratic results were obtained and after a short time the reaction tube broke. It was found that the melted oxides had crept over the sides of the magnesia crucible, made a hole in the bottom of the silver cup and then a hole in the quartz glass. Thallous oxide vapor does not attack silver, for the upper part of the cup was quite clean.

The total volume of the apparatus from the zero mark of the manometer was known to be 57.94 cc. The volume outside the furnace was measured by filling with mercury and weighing. It was found to be 8 cc. The volume in the hot portion was then 49.94 or 50 cc. One centimeter of the manometer contained 0.135 cc. The total volume at room temperature was then 8 + 0.135 times the pressure reading.

Results

In Table I are recorded the oxygen pressures at different temperatures. From the temperatures and volumes of the different parts of the apparatus the number of moles of oxygen at the equilibrium pressures may be calculated. The moles of oxygen will give directly the Tl_2O present, and since the original weight of Tl_2O_3 is known, the mole fraction of Tl_2O may be calculated.

As an example is shown the calculation of the moles of oxygen in equilibrium with a mixture of thallic and thallous oxides at 676°, after the first quantity of oxygen had been withdrawn.

At the beginning of the work, the cup was full of oxygen at atmospheric pressure, which was 0.000692 mole. The first oxygen withdrawn from the system totaled 0.00175 mole. Then actually the difference, 0.001058 mole, was removed from the Tl_2O_3. There was originally 0.01567 mole of Tl_2O_3 present. Then the composition of the mixture before heating to 676° was Tl_2O_3, 0.014612 mole; Tl_2O, 0.001058 mole. At the temperature under consideration the oxygen present was given by the expression

$$N_{O_2} = \frac{p_{O_2}}{R}\left(\frac{V_h}{T_h} + \frac{V_c + V_m}{T_r}\right)$$

where v_h is the volume in the furnace, v_c that outside the furnace up to the zero mark of the manometer, v_m the volume in the manometer, T_h the furnace temperature, T_r the prevailing room temperature and p_{O_2} the oxygen pressure in atmospheres.

$$N_{O_2} = \frac{3.9}{76 \times 82.07}\left(\frac{50}{949} + \frac{8 + 0.527}{295.5}\right) = 0.000051$$

$$\text{Moles of } Tl_2O = 0.000051 + 0.001058 = 0.001109$$

$$\textbf{Mole fraction of } Tl_2O = \frac{0.001109}{0.01567} = 0.0708$$

Thus a solution 7.08 mole per cent. of Tl_2O is in equilibrium with oxygen at a pressure of **3.9** cm. at 676".

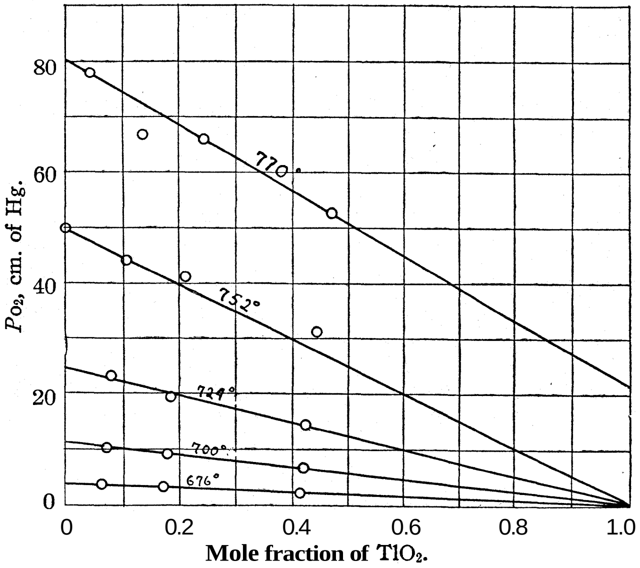

Fig. 3.

From the calculated values of the mole fraction of Tl_2O a pressure–composition diagram was plotted, which is shown in Fig. **3.** The isotherms are apparently straight lines over a long pressure range. By extrapolating these lines to zero mole fraction of Tl_2O, the decomposition pressures of pure Tl_2O_3 are obtained. These values are given in Table II.

The equilibrium constant for the reaction $Tl_2O_3 = Tl_2O + O_2$ may be calculated from these pressures at different temperatures since K_p under these conditions is equal to the oxygen pressure over pure Tl_2O_3. Values of K_p are given. Pressure–temperature curves for any mixture of the two oxides could be constructed from values read from the pressure–composition curves.

TABLE I

OBSERVED DATA

Temp., °C.	Press., cm.	Moles of O_2	Mole fraction of Tl_2O
Moles of Tl_2O_3 originally present, 0.01567; **Moles of O_2 originally present,** 0.000692			
676	19.5	0.000277	...
700	25.6	.000370	...
724	31.7	.000465	...
752	48.8	.000767	0.00479
770	77.8	.00138	.0440
Oxygen removed = 0.00175−0.000692 = 0.001058; **composition of residue (mole fraction of Tl_2O)** = 0.0675			
676	3.9	0.0000510	0.0708
700	10.1	.0001345	.0762
724	23.4	.000330	.0886
752	43.9	.000676	.1109
770	66.4	.001124	.1395
Oxygen removed = 0.00173 **mole; composition of residue** = 0.178			
676	3.3	0.0000429	0.181
700	8.5	.000112	.185
724	18.8	.000258	.1945
752	41.0	.000622	.218
770	66.0	.00111	.249
Oxygen removed = 0.00382 **mole; composition of residue** = 0.422			
676	1.8	0.0000233	0.4232
700	6.4	.0000837	.4270
724	14.2	.000191	.4339
752	20.7	.000443	.4500
770	52.4	.000830	.4760

TABLE II

DECOMPOSITION PRESSURES OF PURE TL_2O_3

Temperature, °K.	949	973	997	1025	1043
Pressure, cm. of Hg	4.2	11.5	25.5	50.0	80.0
K_p, atm.	0.0552	0.1515	0.338	0.656	1.052

TABLE III

VALUES

T, °K.	$-R \ln K$	$1/T$	ΔH	ΔF
949	5.7736	0.001055	77,000	5479
973	3.77436	.001028	71,400	3672
997	2.16942	.001002	77,000	2163
1025	0.3432	.000977	77,000	352
1043	−0.10138	.000958	....	−106

The heat of the reaction within the temperature range studied may be found by plotting $-R \ln K$ against $1/T$, shown in Fig. 4. Four of the five points fall on a straight line. The slope of the line at any point gives the heat of the reaction at that temperature. From the equilibrium constants the free energy of the reaction at certain temperatures was calculated. Values of the heat of the reaction and the free energy are given in Table III.

The Melting Point of Thallic Oxide

Reference to the composition–pressure diagram shows that unless Tl_2O_3 melts below 715–710°, the melting point cannot be determined in air, since the decomposition pressure at 720" is 25.5 cm., while the partial pressure of oxygen in air is about 16 cm. This shows that former determinations must be in error due to the presence of Tl_2O. In addition, former determinations were made in glass, and the silicates formed must have contaminated the oxide.

The determinatioq was carried out in the apparatus illustrated in Fig. 5. This was joined to the system used in the study of the decomposition pressures in the place formerly occupied by the reaction vessel. About 6 g. of black crystalline thallic oxide was placed in a fused magnesia crucible, which had been sealed previously inside a fused quartz bulb. The bulb was joined to the rest of the apparatus by a graded seal. The hot junction of the platinum–platinum-rhodium thermocouple was immersed in the oxide. The wires were insulated by fused quartz beads and led out of the apparatus through seals of de Khotinsky wax.

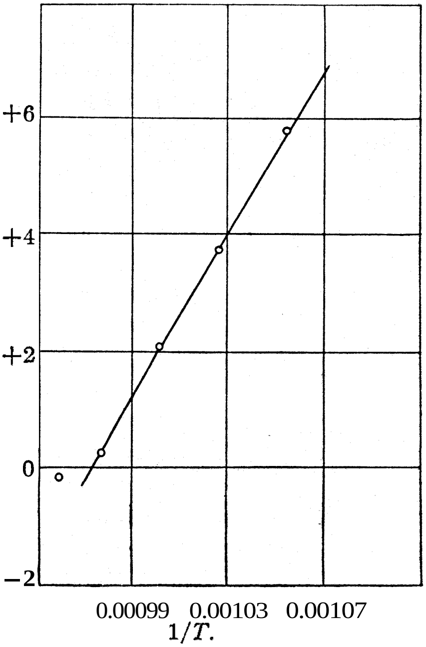

Fig. 4.

An oxygen pressure of one atmosphere was maintained over the oxide during the measurements. Readings of temperature and time were taken and cooling curves plotted. Five determinations were made. The first curve, because of too rapid cooling, showed no break. The next three showed breaks at 715, 717 and 717°. The last showed two breaks, one at 718°, and an indefinite break at about 730". The melting point is considered to be 717 ± 5°.

At the end of the fifth determination the fused quartz tube cracked and the thermocouple wires were found to be badly attacked. This probably accounts for the irregularity observed in the fifth determination.

Discussion

From the results obtained it is evident that the oxygen pressures are dependent not only on the temperature but also on the composition of the mixed oxides in equilibrium with the oxygen. If this were not the case the isotherms would have all been parallel to the composition axis. In this respect the decomposition of thallic oxide differs from the decomposition of silver oxide, mercuric oxide and cupric oxide, in which two condensed phases are present. The decomposition of ferric oxide, barium peroxide and vanadium pentoxide[12,5] gives only one condensed phase, a solid or liquid solution, depending on the temperature. Thallic oxide is to be classed with these latter oxides.

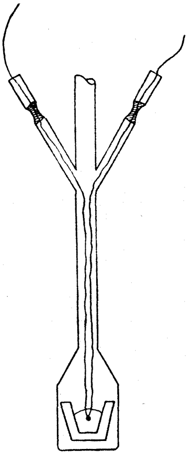

Fig. 5.

It is interesting to note that the isotherms on the pressure-composition diagram are straight lines over large variations in composition. If we apply Raoult's law to this system we find that the ratio of p_{O_2} (which is directly related to the vapor pressure of Tl_2O_3) to the mole fraction Tl_2O_3 is almost constant at constant temperature. Raoult's law seems to be obeyed in this case. This may be due to chemical similarity of the two oxides. Both are basic and show no acidic properties. Although both are polar compounds, the fields of force about the two kinds of molecules may not be different enough to cause wide departures from Raoult's law. In contrast, V_2O_5 is more acidic than basic and V_2O_4, the lower oxide formed by its decomposition, is basic. In the study of the decomposition of V_2O_5 wide variations from Raoult's law were found. We have no evidence that these oxides are associated or dissociated in solution. We have calculated the composition curve assuming that for every mole of oxygen in the gas phase there dissolves one mole of Tl_2O in Tl_2O_3. If either oxide were polymerized, the oxygen pressures would be the same but the mole fractions of Tl_2O differ, giving a different pressure–composition diagram. There seems to be no special reason why this should be the case, but it must be admitted as a possibility.

An examination of the 770° isotherm shows that the best straight line does not cut the 100 mole per cent. Tl_2O line at $p = 0$, as do the other

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[12] Lewis, THIS JOURNAL, **28**, 139 (1906); Keyes and Hara, *ibid.*, **44**, 479 (1922); Hulett and G. B. Taylor, *J. Phys. Chem.*, 17, 567 (1913); Smyth and Roberts, THIS JOURNAL, **42**, 2582 (1920); Sosman and Hostetter, *ibid.*, 38, 807 (1916); Hildebrand, *ibid.*, *34*, 246 (1912).

isotherms. The line may be correct as drawn, indicating dissociation of the lower oxide. There are no data on the dissociation of Tl_2O at these temperatures. Or the line may cut the composition axis at mole fraction $Tl_2O = 1$, and the observed equilibrium values displaced from the true ones because of volatilization of the lower oxide from the solution at this high temperature, which would make the solution less concentrated in Tl_2O than is determined from the oxygen pressures. In general, the 770° isotherm does not seem to be as dependable as the other four. Furthermore, the value of the equilibrium constant obtained from the extrapolation of this curve does not fall on the straight line with the other four as shown in Fig. 4.

It is unfortunate that the heat of reaction and free energy values cannot be extrapolated to low temperatures with any degree of accuracy, but these quantities change very rapidly with temperature and an accurate knowledge of the specific heats and their variation with temperature is needed. Values for Tl_2O_3 could perhaps be determined using a sufficient pressure of oxygen to prevent decomposition, but the determination of the values for Tl_2O at these high temperatures does not seem practicable.

One of the handicaps to this work has been the lack of information about the physical and chemical properties of pure Tl_2O. Indeed, it is doubtful whether pure dry Tl_2O has ever been prepared. Its preparation, purification and any subsequent transference must be carried out in the absence of oxygen and carbon dioxide. This, coupled with its volatile nature at high temperatures, makes a study of the pure oxide very difficult.

In conclusion, the author wishes to express appreciation to Dr. J. C. W. Frazer and to Dr. W. A. Patrick, who suggested this study and under whose direction it was done.

Summary

The equilibrium pressures of oxygen over thallic oxide and mixtures of thallous and thallic oxide have been determined, from which a pressure–composition diagram has been constructed.

The equilibrium pressures of oxygen depend both on the temperature and the composition of the mixture of oxides.

Thallous oxide dissolves in thallic oxide, forming solid and liquid solutions.

The solutions of the oxides appear to obey Raoult's law over the concentration range investigated.

The melting point of thallic oxide has been redetermined, and found to be 717 ± 5°.

Values for the heat of the reaction and the free energy change are calculated for several temperatures.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, OHIO STATE UNIVERSITY]

THE THERMAL DECOMPOSITION OF GASEOUS ETHYLENE OXIDE

BY WINFIELD W. HECKERT AND EDWARD MACK, JR.

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To the rapidly increasing number of homogeneous unimolecular gaseous reactions described in the recent literature, it is the purpose of the present paper to add another, namely, the decomposition of ethylene oxide. This reaction is particularly noteworthy because of the ease with which it lends itself to accurate study, and also because the course of the reaction seems to find an adequate explanation in terms of Christiansen and Kramers' hypothesis.[1]

According to this hypothesis in exothermic reactions the energy with which the freshly formed product molecules are loaded, consisting of the heat of reaction as well as the energy corresponding to the original heat of activation, may be transmitted by collision to unactivated reactant molecules, and thereby maintain a supply of activated reactant molecules, replacing those that have undergone chemical change. An obvious objection to such a mechanism is that the increasing accumulation of inert product molecules, as the reaction progresses, or the introduction of an inert gas into the system, would result in reducing the share of energy obtained by the reactant molecules from the freshly formed product, and hence would cause a much more rapid decrease in velocity than that characteristic of a unimolecular reaction.[2]

As far as the present authors are aware, no unimolecular reaction affected appreciably in this manner by inert product or foreign gas has hitherto been observed. In the case of the decomposition of diethyl ether, Hinshelwood[3] has found that helium and nitrogen have little or no effect, although the reaction products in considerable excess had a slight retarding influence.

Nature of the Reaction.—The decomposition and isomerization (to acetaldehyde) of ethylene oxide in the presence of various catalysts have been studied by Krasussky,[4] Ipatiew and Leontowitsch,[5] Nef[6] and Peytral[7] but in all of these cases the reactions have probably been heterogeneous. We have found that thermal decomposition of ethylene oxide in a pyrex

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[1] Christiansen and Kramers, *Z. physik. Chem.*, 104,451 (1923).

[2] To avoid the difficulty, Christiansen and Kramers made the somewhat forced assumption that the energy-laden product molecules could transmit their energy only to reactant molecules, and not to other molecules,

[3] Hinshelwood, Proc. *Roy. Soc. London,* **114A,** 94 (1927).

[4] Krasussky, J. *Russ. Phys.-Chem. Soc.,* **13,** *34,* 76, 543 (1902).

[5] Ipatiew and Leontowitsch, **Ber., 36,** 2016 (1903).

[6] Nef, **Ann., 335,** 197 (1904).

[7] Peytral, Bull. *soc. chim.,* **39,** *206* (1926).

chamber at 380–444° is a strictly homogeneous gas reaction. This is shown by the data of Table I. The ratio of surface to volume, S/V, was varied more than six times by introducing fragments of pyrex glass tubing into the reaction chamber, without affecting the velocity of the reaction. Furthermore, the reproducibility of the velocity constants indicates clearly that the reaction is homogeneous.

TABLE I

DATA SHOWING THE HOMOGENEITY OF THE REACTION

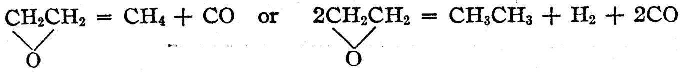
Expt.	P_{av}	Temp., °C.	k_1	S/V	H_2, %
100L	72	443.5	0.0727	8.33	6.6
101L	65	443.5	.0704	8.33	. . .
102L	82	443 5	.0710	8.33	9 9
94–98m, 104–105m, 109–110, 112m	84.5 av.	443 5 av.	0 0720 av.	1 32 av.	7.4 av.

An attempt was made to determine whether acetaldehyde could be isolated from the partially decomposed gases, by passing ethylene oxide through a long tube heated with sulfur vapor. The boiling point of the product was taken by a micro method. The last portions of the product to boil off had a strong aldehyde odor, though hardly that of acetaldehyde. We must conclude that nearly all of the aldehyde, if it is formed at all, is immediately decomposed.

The decomposition of the ethylene oxide was carried on in an apparatus to be described shortly. The product gases were analyzed in a gas analysis apparatus according to the following scheme: dilute sulfuric acid treatment to remove excess ethylene oxide; potassium hydroxide for carbon dioxide; copper oxide at 300° to oxidize hydrogen and carbon monoxide (decrease in volume equals the volume of the hydrogen); potassium hydroxide to remove the carbon dioxide; combustion pipet. The following are some typical analyses.

	Expt. 85K	Expt. 93M	Expt. 87K
H_2, %	6.2	7.8,	7.9
C_2H_6, %	6.6	7.7	7.0
CH_4, %	37.5	35.1	35.3
CO, %	49.6	49.0	49.9

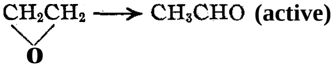
Analyses were also made for hydrogen with palladium black. These checked with the above. Ammoniacal cuprous chloride was used to determine the carbon monoxide in some cases. The ethane was not identified, and all higher hydrocarbons were calculated as ethane. The percentage of hydrogen varied somewhat, but an average of ten experiments gave 7.4. No factor, surface, temperature, pressure, etc., could be found which determined the percentage of hydrogen. It would appear, therefore, that the reaction occurs in two ways with perhaps acetaldehyde as an intermediate compound.

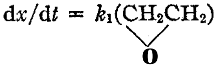

$$\underset{O}{CH_2CH_2} = CH_4 + CO \quad \text{or} \quad 2\underset{O}{CH_2CH_2} = CH_3CH_3 + H_2 + 2CO$$

In any case, at the completion of the reaction, the pressure is just doubled.

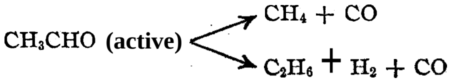
	Expt. 107M	Expt. 108M
Initial pressure, cm.	30.92	23.21
Final pressure, cm.	61.86	46.42

There is considerable evidence that the decomposition of ethylene oxide is not as simple as it is represented above. There is a perceptible induction period. This lasts for a period of about one and one-half minutes at 444°, and for nearly fifteen minutes at 400°. During this time the velocity increases. The induction period is followed by a period when the unimolecular law holds quite accurately. At still later stages the velocity falls off due to the accumulation of reaction products, methane and carbon monoxide. Other inert gases are shown to have a similar retarding effect. The fact that ethylene oxide isomerizes so readily to give off 23,300 cal.[8] per mole, together with the facts above, leads us to postulate the following mechanism.


$$\underset{O}{CH_2CH_2} \longrightarrow CH_3CHO \text{ (active)} \qquad (1)$$


$$dx/dt = k_1(\underset{O}{CH_2CH_2})$$

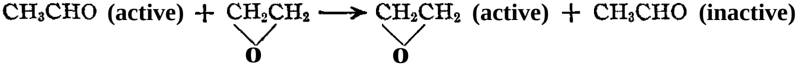
$E = 52{,}000$ cal.
$Q = 23{,}300$ cal.
75,300 cal.


$$CH_3CHO \text{ (active)} \begin{cases} \nearrow CH_4 + CO \\ \searrow C_2H_6 + H_2 + CO \end{cases} \qquad (2)$$

$$dx/dt = k_2\ (CH_3CHO)\ \text{(active)}$$

E and Q very small

$$CH_3CHO\text{(active)} + X \longrightarrow CH_3CHO \text{ (inactive)} + X \text{ (energy-laden)} \qquad (3)$$


$$CH_3CHO \text{ (active)} + \underset{O}{CH_2CH_2} \longrightarrow \underset{O}{CH_2CH_2} \text{ (active)} + CH_3CHO \text{ (inactive)}$$

$$2CH_3CHO \longrightarrow 2CH_4 + 2CO \qquad (4)$$

Hinshelwood and Hutcheson[9] have shown that acetaldehyde decomposes bimolecularly in the neighborhood of 444°. The energy of activation was found to be 45,500 cal. for two moles. Acetaldehyde molecules, if formed by the above mechanism, would have about 75,000 cal. per mole, or more than three times the amount necessary for activation. They would probably decompose unimolecularly under these conditions, and collisions with inert molecules would tend to cause them to lose some of their large load of energy. According to the theory of Rice and Ramsperger, or that of

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[8] Estimated from the heats of combustion given by Berthelot: for ethylene oxide, 6870 cal./g., *Ann. chim. phys.*, [5] 27, 374 (1882); for acetaldehyde, 6338 cal./g., *Compt. rend.*, 129, 920 (1899).

[9] Hinshelwood and Hutcheson, *Proc. Roy. Soc. London*, 118A, 380 (1926).

Kassel, the loss of this energy would lower their rate of decomposition until finally the reaction would be of the second order. Collision with ethylene oxide molecules would perhaps result in the activation of the latter. This would not reduce the rate.

If we consider the first two reactions above and integrate the differential equation for the successive reactions, we obtain the following equation

$$\frac{a - x}{a} = \frac{k_2}{k_2 - k_1} e^{-k_1 t} - \frac{k_1}{k_2 - k_1} e^{-k_2 t}$$

where $a - x$ is the partial pressure of the ethylene oxide at the time t. The application of this equation is somewhat difficult. However, in the present case k_2 is large and k_1 is small. Hence, immediately following the induction period, the second term on the right drops out and we obtain the following expression for k_1

$$\frac{a - x_1}{a - x_2} = e^{-k_1 t_1}/e^{-k_1 t_2}$$

$$k_1 = \frac{2.303}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$$

This may then be used to calculate k_2

$$k_2 = \frac{k_1 Y_2}{Y_2 - e^{-k_1 t_2}},\quad Y_2 = (a - x_2)/a$$

The time t_2 must be taken such that $k_1 e^{-k_2 t_2}/(k_2 - k_1)$ has become vanishingly small.

Having obtained a value for k_2, it is now possible to calculate values for k_1 over the entire interval.

$$k_1 = \frac{2.303}{t} \log \frac{A}{Y_t + Be^{-k_2 t}}$$

where

$$A = k_2(k_2 - k_1),\quad B = k_1(k_2 - k_1)$$

The values of k_1 calculated in this manner and shown in Table II and IIA are very satisfactory. Without this treatment of the decomposition as a two-stage reaction, the constant k_3, calculated directly from the pressure data by the classical unimolecular equation, is found to vary by several hundred per cent., at least at those lower temperatures where the induction period is long enough to be followed.

It is possible to consider the induction period as merely due to the building up of a number of "reaction chains" as demanded by the Christiansen-Kramers theory. On such an hypothesis the energy-laden products would activate ethylene oxide molecules by collision with them. Such a picture, as previously indicated, would agree qualitatively with the experimental data. It seems certain that an intermediate state of some nature occurs during the reaction.

Measurement of Reaction Velocity.—A number of different samples of ethylene oxide were used, all of which gave the same velocity constant. Most of the samples were prepared by distilling an Eastman Kodak product at least three times over freshly burned calcium oxide. Low-boiling fractions were retained, giving a final sample boiling from 9.95–10.00° (corrected). This is two degrees lower than the boiling point reported in the literature.

The sample was kept in the dark in Bulb B in cold water, Fig. 1. Ethylene oxide was found to decompose slowly at room temperature. A sample taken from an old iron tank was 18% unabsorbed by sulfuric acid; this unabsorbed portion analyzed 50% of carbon monoxide. To avoid any error due to such decomposition, the storage tank S was pumped out before each run.

The apparatus, shown in Fig. 1, was the conventional set-up. Constant temperature was secured by boiling sulfur in the jacket J, where the pressure was controlled by the height of the water in the tube N. The five-gallon carboy G was connected to a pump which operated at a rate sufficient to pull an occasional bubble through the tube N. The outer jacket was heated by an auxiliary electric furnace, maintained at about 300°. The sulfur was boiled with a Fischer burner. The upper end was cooled with an air blast and several turns of lead pipe supplied with cold water. The whole lower part was enclosed in an asbestos box.

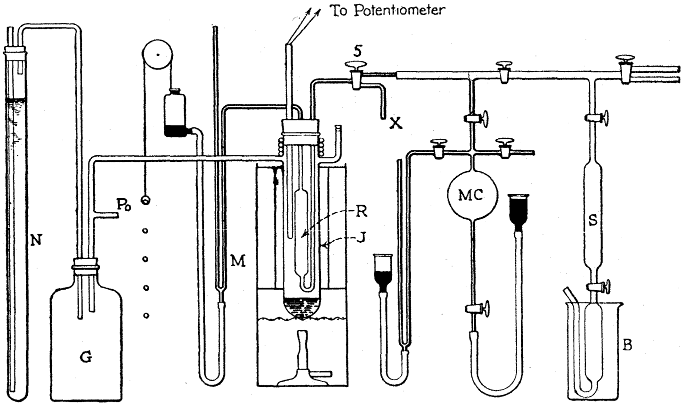

Fig. 1.

The temperature was measured with a calibrated chromel–alumel thermocouple and a potentiometer. It was possible to measure changes in temperature of 0.1°. The absolute temperatures are probably correct to within 0.5°.

The reaction chamber R was blown from pyrex tubing. It was connected to the stopcock 5 by means of 1-mm. tubing, and to the manometer M with 1.5-mm. capillary. The manometer M was made from 2-mm. capillary. The left arm was 2 meters long; the right, 1 meter long. The mercury leveling bulb was maintained at such a height that the right column could be read within 10 cm. of the top of the manometer arm. Thus the total dead space varied between 0.6 and 0.9 cc. This usually represented about 0.3% of the volume of the reaction chamber. The meter stick in the manometer was compared with a standard meter stick. The apparatus was frequently cleaned by pumping hot chromic acid through it. It was washed with distilled water, acetone and ether. A vaseline–paraffin mixture was used on all of the stopcocks. Stopcock 5 was enclosed in a metal container and surrounded with water maintained at a suitable temperature.

For experiments dealing with the effect of inert gases, a chamber, MC, was attached, in which it was possible to mix the gases thoroughly before passing them into the reaction chamber. A water jacket, not shown in the drawing, maintained a constant temperature while filling the mixing chamber.

The procedure in making a run was briefly as follows. The reaction chamber was evacuated with an oil pump and stopcock 5 was closed. The chamber S and the connecting tubes were evacuated and filled with ethylene oxide. Stopcock 5 was opened and zero time was counted (with a stop watch) when one-half of the desired amount of ethylene oxide had entered. The bulb was raised until the mercury stood within a few centimeters of the top of the right arm of the manometer. Readings on both arms were taken as desired. If it was desired to analyze the gases, they were removed at X. The temperature and barometric pressure were read at frequent intervals.

The total pressure P_1 was calculated from the manometer readings. From this the total pressure P_2, if there had been no dead space, was calculated by means of the equation

$$P_2 = P_1(1 + vT_R/VT_m)$$

where v is the dead space to the top of the mercury, V is the volume of the chamber, T_m is the temperature of the manometer and T_R that of the

TABLE II

COMPLETE DATA FOR EXPERIMENT 168m AT 378.5°

Time, minutes	V	P_{at}	Manometer readings Left	Manometer readings Right	P_I	Correction	Pa	$a - x$	$k\sim$	ka	ka
0	0.015752	73.92	21 00	94.62	....	..	107 42	106 36	....		
1	....		128.78	95.73	106 67	0.79	107.46	106 32	....		
1	.....	...	....	95 61	106.79	.79	107 58	106 20	0.00223	..	0.00076
5	....			95 28	107 22	.80	108 02	105 76	.00242	..	.00113
10	,015752	...	....	94 62	107.88	.84	108 72	105 06	,00219	..	.00123
20	.....	...	....	93 19	109.21	.89	110.10	103 68	,00187	..	.00128
30	....			91 26	111.14	.98	112 12	101 66	,00192	..	.00150
45	....		134 66	94 18	114.10	.89	114 99	98 79	,00192	..	.00164
60	....			91.57	116 71	1 01	117.72	96 06	.00191	0.15	.00170
75	.015746	..	...	89.06	119 22	1.06	120 28	93 50	.00189	..	.00272
90	....		142.68	94.51	121 89	0 93	122.82	90.96	.00188	..	.00174
105	.....	73 92	....	92 21	125 19	1.05	125.24	88 54	,00187	..	.00175

TABLE IIA

VELOCITY CONSTANTS POR EXPERIMENT 125m AT 414.5°

Time, minutes	P_2	$a - x$	k_1	k_2	ka
0	116.51	115.30	...	...	...
$^1/_2$	116 76	115.05	...	...	...
1	117.18	114.63	0.0162	...	0.00506
2	118.19	113.62	.0150	...	.00732
3	119.60	112.21	.0149	...	...
4	121.00	110.81	.0146	...	...
5	122.56	109.25	.0146	...	.0108
6	124.12	107.69	.0147	...	...
7	125.72	106.09	.0147	...	...
8	127.39	104.42	.0149	...	...
9	128.74	103.02	.0147	...	...
10	130.31	101.50	.0147	...	.0128
11	131.78	100.03	.0147	...	...
12	133.23	98.58	.0147	...	...
13	134 70	97.11	.0147	0.753	...
18	141.37	90.44	.0143	...	.0135

reaction chamber. Since the pressure just doubles, the final pressure would be $2P_2$, providing all of the ethylene oxide in the manometer were to decompose. In order to estimate the partial pressure P_0 of the ethylene oxide actually in the chamber, the following equation was used

$$P_0 = 2(P_2)_0 - P_2\frac{3v_0T_R}{2VT_m} - (P_2)t$$

At best this is an approximation. However, the error probably at no time exceeds $0.5v_0T_R/VT_m \cdot P_2$, which represents an error of 0.5% or less.

Ethylene oxide is not associated in the vapor phase.

Order of Reaction.—The decomposition of ethylene oxide is a first-order reaction without question. Table III gives values of k_1 taken over a large range of pressures.

TABLE III

VELOCITY CONSTANT k_1 AT DIFFERENT PRESSURES

Expt.	Temp.. °C.	P_{av}., cm.	k_1	$k_1(444)$
142m	443.1	90.5	0.0707	0.0739
145m	443.1	96.0	.0709	.0741
146m	443.5	64.7	.0716	.0735
147m	443.6	59.9	.0719	.0736
155m	444.0	28.5	,0666	.0666
162m	443.7	2.42	.0617	.0627

If the reaction were bimolecular, k_1 calculated at an interval averaging a pressure of 2.42 cm. would be enormously smaller than at 96.0 cm- These constants were calculated over the two to five-minute interval immediately following the induction period.

The induction period becomes more noticeable as the temperature is lowered. It is impossible to evaluate k_2 at 444'. At 394° values can be calculated, but the error is large.

TABLE IV

VELOCITY CONSTANT k_2 AT DIFFERENT PRESSURES (T = 394.3°)

Expt.	P_{av}.	k_1	k_2
169m	83.9	0.00486	0.353
170m	41.5	.00474	.472
171m	21.3	.00471	609
172m	11.8	.00464	Too large to calculate
250m	52.9	.00473	.495
251m	31.8	.00475	.654
253m	17.1	.00454	Too large to calculate

Apparently k_2 becomes larger with decrease in pressure. This is in agreement with the mechanism advanced, since the decomposition of activated acetaldehyde molecules is more likely to take place when there is a greater time between deactivating collisions.

In Fig. 2 the results of a number of experiments at approximately 444° are shown. The logarithm of the partial pressure of the ethylene oxide is plotted against time, with the logarithm scale shifted to bring all of the experiments together. The falling off of the rate with accumulation of products is clearly shown. This is not proportional to the pressure of the products, but more nearly to the ratio of their pressure to that of the ethylene oxide. After a steady state has been reached, the pressure of activated acetaldehyde molecules will be nearly proportional to the partial pressure of the undecomposed ethylene oxide. Since the first point on these graphs must be estimated, the nature of the induction period at this temperature must remain unknown.

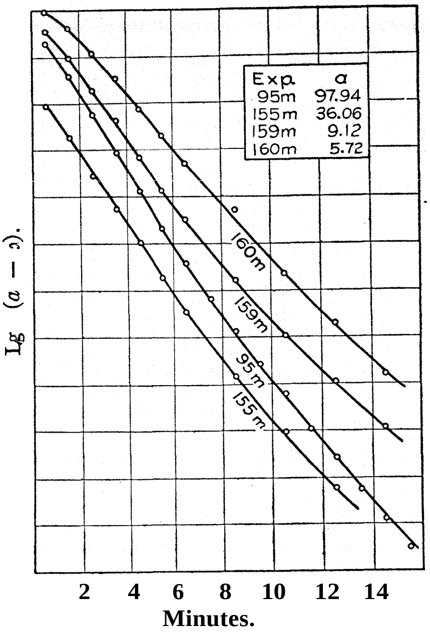

Fig. 2.

Energy of Activation.—Table V gives a summary of the data (at the higher pressures) from which the energy of activation may be calculated. Figure 3 shows a plot of $-\log k_1$ against $1/T$. The usual straight line is obtained. The energy of activation E, calculated by equating the slope of this line to $E/2.303R$, is 52,000 cal.

TABLE V

VELOCITY CONSTANT k_1 AT VARIOUS TEMPERATURES

Expt.	Temp., °C.	k_1	Expt.	Temp., °C.	k_1
199m	444.8	0.0793	120m	425.1	0.0251
142m	443.1	.0707	121m	425.2	.0265
143m	443.1	.0709	122m	424.7	.0281
144m	443.1	.0702	124m	414.4	.0154
145m	443.1	.0709	125m	414.5	.0147
134m	442.4	.0668	140m	411.6	.0131
135m	442.4	.0693	141m	411.6	.0130
136m	442.4	.0663	130m	399.1	.00622
137m	442.3	.0670	131m	397.7	.00573
138m	434.8	.0458	132m	396.8	.00542
139m	424.0	.0249	169m	394.1	.00484
			168m	378.5	.00191

The Effect of Inert Gases.—It was thought that a study of the rate of decomposition of ethylene oxide in the presence of a number of inert gases would yield some interesting information with regard to the exchange of energy during collision. Table VI gives a summary of the experimental data. Traces of oxygen interfere with the observation of the induction period and give false values for k_2.

In Table VI $P_{\text{av.}}$ is the average partial pressure of the ethylene oxide during the interval in which k_1 was calculated. The column headed P_g is the partial pressure of the inert gas. The column P_{CO} is one-half of the average pressure of the products during the interval. All of the experiments are corrected over short temperature intervals to 394.3°.

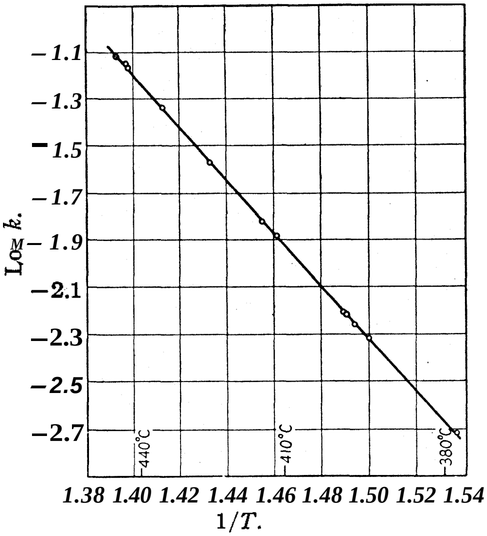

Fig. 3.

In addition to those listed in the table, ethylene, ammonia, methyl bromide, n-butane and isopentane were tried. In the first case there was probably a polymerization of the ethylene and a combination with the ethylene oxide. Ammonia apparently reacted somewhat with the oxide while in the mixing chamber, and the resulting compound dissociated during the first several minutes of the experiment. This suggests that the decomposition of aminoethyl alcohol might yield another unimolecular reaction. Methyl bromide, n-butane and isopentane were found to "crack" in the presence of ethylene oxide. The velocity of "cracking" was greater in the presence of ethylene oxide than in its absence, which suggests that these substances were obtaining energy of activation from the ethylene oxide decomposition.

The two sets of experiments on carbon dioxide indicate that within the limits of experimental error the depression of k_1 is proportional to the ratio of pressure of the inert gas to that of the ethylene oxide.

In the case of the hydrocarbons, it is at once apparent that the depression of the velocity constant is related to the complexity of the molecule. The isosteres, nitrogen and carbon monoxide, both cause the same depression. Carbon dioxide, with several more degrees of freedom and a larger collision area, though with a smaller velocity of translation, exhibits a slightly greater depression.

Argon and neon depress the rate less than any of the other gases. Their collisions are perhaps the most elastic and they have but three degrees of

TABLE VI

EFFECT OF INERT GASES (T = 394.3°)

Expt.	$P_{av.}$	P_g	P_{CO}	k_1	k_2
Blank (average)	31.8	..	4.4	0.00473	0.654
		Carbon Dioxide			
175m	29.4	69.4	3.6	.00423	.345
176m	30.4	71.9	3.7	.00422	.389
177m	31.9	75.4	3.8	.00420	.340
	30.6	72.2	3.8	,00422	.358
248m	32.1	37.1	4.1	.00445	.355
249m	32.0	37.0	4.1	,00437	.449
	32.1	37.1	4.1	.00441	.402
		Carbon Monoxide			
193m	30.9	72.5	4.0	.00431	.420
194m	31.9	74.8	4.1	.00429	.421
195m	30.4	71.2	3.9	,00429	.346
	31.1	72.6	4.0	.00430	.396
		Nitrogen			
183m	28.3	67.9	3.8	.00432	.395
184m	30.7	70.7	3.8	.00429	,419
185m	31.1	71.3	3.7	.00430	.287
189m	31.0	72.6	4.0	.00431	.433
190m	33.3	77.5	4.2	.00427	.404
	30.8	72.0	3.9	.00430	.388
		Methane			
240m	32.4	72.7	3.4	.00402	.296
241m	32.2	73.3	3.8	.00407	.369
242m	31.3	74.9	3.8	.00413	.385
243m	30.9	73.4	3.5	.00407	.319
	31.7	73.6	3.6	.00407	.342
		Ethane			
222m	31.3	72.7	3.5	,00347	1.16"
224m	30.7	71.9	2.9	.00346	0.236
225m	31.5	73.8	3.0	.00355	.217
226m	31.5	73.6	3.0	.00344	.259
	31.2	73.0	3.1	.00348	.237
		Propane			
228m	32.7	75.0	3.0	.00339	.271
229m	32.2	73.8	3.0	.00331	.257
231m	30.6	72.4	3.1	.00341	.507[a]
	31.8	73.7	3.0	.00337	.264

TABLE *VI* (*Concluded*)

Expt.	$P_{av.}$	P_g	P_{CO}	k_1	k_2
		*Iso*butane			
214m	30.5	71.8	3.0	.00283	.315
215m	30.0	71.0	3.1	.00286	.495
216m	32.0	74.6	2.8	.00280	.480
	30.8	72.5	3.0	.00283	.430
		Argon			
255m	31.8	71.5	4.2	.00450	.644
256m	32.4	72.8	4.2	.00447	.445
	32.1	72.1	4.2	.00449	.544
		Helium			
257m	32.2	70.1	3.9	,00415	.377
258m	32.6	70.9	3.9	.00420	.355
	32.4	70.5	3.9	.00418	.366
		Neon			
259m	31.4	72.3	4.4	.00456	.503
260m	32.0	72.7	4.1	.00441	.329
	31.7	72.5	4.3	.00449	.416

[a] Not included in average.

freedom (translational). Helium, however, depresses the rate considerably.

The **Effect** of Hydrogen.—While investigating the decomposition of di-ethyl ether at low pressures, Hinshelwood and his students have shown that the presence of sufficient hydrogen will restore the high pressure rate of decomposition. They attributed this to the fact that hydrogen, traveling at high velocities and making many collisions, was peculiarly fitted for maintaining the Maxwellian distribution of energy among the decomposing molecules. No other gas was found to have this effect.

TABLE VII

THE EFFECT OF HYDROGEN

Expt.	Temp., °C.	$P_{av.}$	P_{H_2}	k_1	k_2
190m	394.3	28.4	74.0	0.00700	1.02
191m	394.3	28.8	72.6	.00716	.53
192m	394.3	28.8	75.7	.00714	1.43
	394.3	28.7	74.1	.00710	
196m	444.6	24.4	76.2	.110	
197m	444.8	23.5	74.4	.111	
198m	444.9	25.6	80.9	.109	
	444.8	24.5	77.2	.110	

E = 51,500 cal.

Table VII shows a number of results of experiments with ethylene oxide in the presence of about one atmosphere of hydrogen. The rate is increased about 40% at each temperature. The heat of activation calculated on the basis of these experiments is 51,500 calories, the same as before within the limits of experimental error.

Study of the decomposition of ethylene oxide is being continued at much lower pressures to collect sufficient data for testing the validity of the Rice and Ramsperger equations.

We wish to express our gratitude to the E. I. du Pont de Nemours Company for a Fellowship grant which made this investigation possible.

Summary

It has been shown that the thermal decomposition of ethylene oxide is a strictly homogeneous unimolecular reaction, exhibiting an induction period and a decrease in rate of decomposition in the presence of inert gases. The velocity of decomposition may be represented by the equation

$$\ln k_1 = 34.02 - 52{,}000/RT$$

A mechanism for the decomposition has been advanced involving a unimolecular isomerization to acetaldehyde molecules of high energy content and their subsequent unimolecular decomposition into carbon monoxide and methane. Collision of activated acetaldehyde molecules with inert gases and the consequent interference with the Christiansen-Kramers mechanism for activation, have been regarded as the cause of the damping effect of inert gases. A study of the velocity of decomposition has been made in the presence of ten inert gases. The fact that the presence of hydrogen increases the velocity of decomposition, together with a slight falling off of the velocity constant with decrease in pressure, has been cited as evidence that the reaction at ordinary pressures is in a process of change from a unimolecular reaction to a bimolecular reaction.

COLUMBUS, OHIO

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 221]

THE IONIZATION CONSTANT OF PARA-CYANOBENZOIC ACID

BY EDGAR P. VALBY AND HOWARD J. LUCAS

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It has been pointed out by one of us[1] that from the ionization constants of the para-substituted benzoic acids it is possible to obtain an approximate value of the relative electron attractions of radicals. It has been assumed that in such acids the substituent groups are so far removed in space from the carboxyl group that their effect upon the latter is largely the result of electron displacements through the benzene ring and not of electrostatic influences operating across space. It is therefore desirable to know the ionization constants of all of the para-substituted benzoic acids. In this paper are described the methods by which *p*-cyanobenzoic acid was prepared and its ionization constant determined.

In the process of replacing amino by cyano it is necessary to avoid, first, the formation of *anti*-diazocyanide,[2] second, the decomposition of the sodium cuprous cyanide when the acid, which is present in the diazotized solution, is added and, third, the hydrolysis of the cyano group in the final product. As the replacement reaction is not especially rapid it was found necessary to maintain a temperature of 50–60°. Since *syn*-diazotates may at this temperature change to the stable anti-forms, it was thought best to keep the diazo solution acid until it could react with the cuprous cyanide. The addition of sodium carbonate to the cuprous cyanide solutions,[3] following a procedure which had been developed previously in this Laboratory in connection with other work,[4] seemed to overcome these difficulties fairly well, since the yield of crude *p*-cyanobenzoic acid, m. p. 206–210° (uncorr.), was 45%, and of the pure acid, m. p. 218.5–219° (corr.), after five crystallizations from hot water was 30%.[5]

From measurements on the conductance of aqueous solutions of the pure p-cyanobenzoic acid the ionization constant has been found to be

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[1] Lucas, THIS JOURNAL, 48, 1837 (1926).

[2] Hantzsch and Schulze, *Ber.*, 28, 666 (1895), showed that the anti-diazocyanides are stable and do not readily decompose to yield nitriles.

[3] "Organic Syntheses," John Wiley and Sons, 1925, Vol. IV, p. 69. In the preparation of the tolunitriles sodium carbonate is added to the cold solution of the diazotized amine. The modification here described is more convenient.

[4] E. D. Stewart, "Senior Thesis," California Institute of Technology, 1925.

[5] Sandmeyer, *Ber.*, 18, 1497 (1885), reported that the acid is unstable and changes into terephthalamide upon crystallization from hot water. However, Kattwinkel and Wolffenstein, *ibid.*, 34, 2423 (1901), showed that the cyano acid can be prepared by the Sandmeyer method and can be recrystallized from hot water to give a product melting at 219°.

3.1×10^{-4}, the calculation being made according to the usual expressions

$$K_A = \frac{c\gamma^2}{1 - \gamma}$$

where $\gamma = \Lambda_c/\Lambda_0$, Λ_0 = the conductance at zero concentration and Λ_c = the conductance at the concentration c.

A comparison of the ionization constant of this acid with those of other para-substituted benzoic acids indicates that CN has a lower electron attraction than NO_2 and a greater one than SO_2NH_2, since the constant of *p*-$C_6H_4NO_2COOH$ is 4.0×10^{-4} and that of *p*-$C_6H_4SO_2NH_2COOH$ is 2.6×10^{-4}.

The solubility of p-cyanobenzoic acid is approximately 0.12 g. in 100 g. of water at 20° and 4 g. at 100°.

Terephthalamide, produced by the action of hydrogen peroxide on *p* cyanobenzoic acid,[6] has such a low solubility that no measurements of its conductivity were undertaken.

***p*-Cyanobenzoic** Acid.—An alkaline solution of sodium cuprous cyanide is first prepared by adding the cuprous chloride obtained from 160 g. of copper sulfate[7] to a solution of 80 g. of sodium cyanide in 125 ml. of water,[3] followed by the addition of 60 g. of anhydrous sodium carbonate. To the resulting liquid, maintained at a temperature of 50–60°, is added during the course of ten to fifteen minutes the diazotized solution obtained from 40 g. of *p*-aminobenzoic acid, 70 g. of concd. hydrochloric acid (*c.* P.), 100 g. of water, 300 g. of ice and 20 g. of sodium nitrite (in 50 g. of water). The mixture is maintained at 50–60° for about half an hour, by which time the evolution of nitrogen has practically ceased. It is then cooled and concd. hydrochloric acid is added until no more precipitate comes down. The solid, consisting of p-cyanobenzoic acid and cuprous cyanide, is filtered off, washed and treated with about 75 ml. of concd. ammonium hydroxide, which forms the soluble ammonium salt of the organic acid. The solution is filtered from insoluble copper salts and the p-cyanobenzoic acid is precipitated as a brown mass on the addition of hydrochloric acid to the filtrate. The product has a melting point of 206–210°; yield, 45%.

Five crystallizations from hot water to which animal charcoal has been added give white plates melting at 218.5–219° (corr.); yield, 30%.

The equivalent weight of the acid was determined by titration of 40.00 ml. of a solution made by dissolving 0.5006 g. in 500 ml. of water at 20° against 0.01660 N barium hydroxide. The mean of five titrations gave 16.457 ml. of the base, from which the calculated equivalent weight is 146.6. The theoretical value is 147.1.

The Conductance Measurements.—These were determined by the method of Kohlrausch, employing, however, an a. c. galvanometer for detecting balance instead of a telephone receiver. The cell was immersed in a thermostat at 25°. The results obtained are shown in the accompanying table.

Calculation of the Ionization Constant. In using the equivalent conductance at zero concentration we have adopted the value of 377 reciprocal ohms, which is the one previously found for *m*-cyanobenzoic

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[6] Kattwinkel and Wolffenstein, *Ber.*, **37,** 3221 (1904).

[7] "Organic Syntheses," John Wiley and Sons, **1923,** Vol. III, p. 33.

TABLE I

CONDUCTANCE MEASUREMENTS ON *p*-CYANOBENZOIC ACID AT 25° ±0.02 (CELL CONSTANT = 0.186)

Expt.	Concn., moles/liter	Resistance in ohms	Λ_c	Λ_c/Λ_0	$K_A \times 10^{-5}$
1	0.007446	352.9	70.79	0.1878	32.2
2	.006936	367.5	72.97	.1936	32.2
3	.006906	369.6	72.48	.1932	32.0
4	.004141	494.0	90.92	.2412	31.7
5	.002059	755.3	119.6	.3172	30.4
6	.0008235	1347.0	167.7	.4448	29.4
				Mean	30.9

acid.[8] The assumption that isomeric m- and *p*-cyanobenzoic acids have the same equivalent conductance at zero concentration is warranted from a comparison of other isomeric *m*- and p-substituted benzoic acids.[8] If we take the equivalent conductance of hydrogen ion at 25° to be 350 reciprocal ohms,[9] the equivalent conductance of p-cyanobenzoic ion is then 27, a value which checks well with that of caproate ion, 27.4.[10]

Summary

By a 'modification of the Sandmeyer method p-cyanobenzoic acid may be obtained in satisfactory yields from p-aminobenzoic acid.

The ionization constant of p-cyanobenzoic acid as determined by conductivity measurement has a mean value of 3.1×10^{-4} at 25°.

On the assumption that the ionization constants of *p*-substituted benzoic acids are directly related to the electron attraction of radicals, the electron attraction of CN is greater than that of SO_2NH_2 and less than that of NO_2.

PASADENA, CALIFORNIA

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[8] Ostwald, Z. *physik. Chem.,* 3, 241 (1889), reports a value of 354 expressed in Siemens or mercury units. Compare Scudder, "Conductivity and Ionization Constants of Organic Acids," John Wiley and Sons, New York, 1914, p. 489.

[9] Kraus and Parker, THIS JOURNAL, 44, 2429 (1922), obtain the value 349.93 at 25°.

[10] Creighton and Fink, "Electrochemistry," John Wiley and Sons, Inc., New York, 1924, p. 137.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, MICHIGAN AGRICULTURAL EXPERIMENT STATION]

THE DETERMINATION OF ALUMINUM IN PLANTS. I. A STUDY OF THE USE OF AURINTRICARBOXYLIC ACID FOR THE COLORIMETRIC DETERMINATION OF ALUMINUM[1]

BY O. B. WINTER, W. E. THRUN AND O. D. BIRD

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Two types of methods, colorimetric and spectrographic, have been used for determining very small amounts of aluminum. The latter is of very recent origin. It has one decided advantage over other methods in that it requires no chemical reagents, a point which is particularly important in the estimation of aluminum since this element contaminates nearly all reagents. Unfortunately the necessary apparatus is so expensive that but few laboratories can afford to possess it.

Though known for many years, colorimetric methods for estimating aluminum have only recently assumed importance as the increased demand for micro methods has aroused interest in colorimetric methods in general. While affording many chances for inaccurateness, they can be used wherever a colorimeter is available and hence have tempted chemists to work for their perfection. Several such methods have been proposed, the most promising of which is the one making use of the ammonium salt of aurintricarboxylic acid—the dye commercially known as aluminon. Lundell and Knowles[2] used it for the detection of small amounts of aluminum in certain non-ferrous materials; Myers and co-workers[3] used it for the determination of aluminum in blood and animal materials, while Yoe and Hill[4] studied the reaction of aluminum with the dye under different experimental conditions and discussed its application to the colorimetric determination of aluminum in water. Some time previous to the above, Hammett and Sottery[5] studied the behavior of some of the common elements and ions with the dye, and Middleton[6] and Corey and Rogers[7] studied its behavior with some of the less common elements.

Yoe and Hill showed that during the formation of the aluminum lake intensity of color increased, within certain limits, with rise in tempera-

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[1] Published by permission of the Director of the Experiment Station as Journal Article Number 7 (n. s.) and Number 48 from the Chemical Laboratory.

[2] Lundell and Knowles, *Ind. Eng. Chem.*, **18**, 60 (1926).

[3] Mull, Morrison and Myers, *Proc. Soc. Exptl. Biol. Med.*, 24, 476 (1927); Myers, Mull and Morrison, *J. Biol. Chem.*, 78, 595 (1928); Myers and Mull, *ibid.*, 78, 605 (1928); Myers and Morrison, *ibid.*, 78, 615 (1928); Myers and Mull, *ibid.*, 78, 625 (1928).

[4] Yoe and Hill, THIS JOURNAL, **49**, 2395 (1927).

[5] Hammett and Sottery, *ibid.*, **47**, 142 (1925).

[6] Middleton, *ibid.*, 48, 2125 (1926).

[7] Corey and Rogers, *ibid.*, 49, 216 (1927).

ture, length of time of standing and with the increase in the quantity of aluminum, dye, hydrochloric acid or ammonium acetate present. They also showed that the color decreased with increase in volume of solution and with the amount of ammonium hydroxide or carbonate added, and that the use of protective colloids made it possible to increase the concentration of the lake without having it precipitate.

Several attempts at determining aluminum in plants by the modifications of the method used by these investigators showed that none was entirely satisfactory in our, hands. The following difficulties were encountered.

(1) The results of duplicate determinations did not always agree. (2) The color of some samples faded rapidly. (3) The necessity of having the amount of aluminum in the standard nearly the same as that in the sample required the preparation of several standards whenever a number of determinations were to be made. This wasted much time.

Hence it was decided to make a further study of the reaction between aluminum and the dye in an attempt to overcome these difficulties and if possible to adapt the method to our problem. Special emphasis was placed on determining suitable conditions (1) for the formation of a lake of maximum color intensity and (2) for destroying the color of the excess dye while retaining the lake color. Considerable time was also given to working out a procedure whereby the relationship between the amount of aluminum in a sample and the colorimeter readings could be represented by a curve. This would enable the analyst to compare all of the samples run at one time with one standard and to read the amount of aluminum directly from this curve.

Experimental Part

Apparatus and Reagents.—The lakes were developed in 50-cc. volumetric flasks. The colors were compared in a Duboscq type of colorimeter using a daylight lamp in a dark room or ordinary daylight. The reagents used in the preliminary work were not standardized but were approximately as follows: (1) hydrochloric acid, 1.5 N; (2) ammonium acetate, 5 *N;* (3) ammonium carbonate, 3 *N;* (4) ammonium hydroxide, N and 5 N; (5) 10% ammonium carbonate in ammonium hydroxide (1–2); (6) ammonium salt of aurintricarboxylic acid, 0.1 and 0.2%; (7) standard aluminum solution. This was prepared by dissolving 1.0000 g. of aluminum metal (99.976% Al) in as little hydrochloric acid as possible, diluting to 1 liter with distilled water, taking 10 cc. of this solution and again diluting to 1 liter. Each cc. of this final solution contained 0.01 mg. of aluminum. The reagents used in the later work were standardized and were as follows: (1) hydrochloric acid, 1.5 *N;* (2) ammonium acetate, 5 *N;* (3) ammonium carbonate, 3.2 *N;* (4) ammonium chloride, 5 *N;* (5) standard aluminum solution, same as above.

Color Development

The Dye.—Before attempting to find the optimum conditions under which a lake of maximum color could be obtained, it was deemed advisable to make a similar study of the dye alone.

To ascertain the effect of acidity on the dye several samples of varying *PH* were prepared by adding hydrochloric acid to distilled water, then adding 2 **cc.** of 0.1% dye to 25 cc. of these solutions and allowing them to stand for forty-five minutes for the color to develop. The *PH* of each solution was determined colorimetrically using phenol red, the color intensities were compared with the standard described above and calculated to a uniform basis giving the standard an arbitrary value of 100. The results are shown in Table I.

TABLE I

COLOR INTENSITY OP DYE AT DIFFERENT PH READINGS

Solution	1	2	3	4	5	6	7	8	9
PH	6 9	6.0	5 5	4 9	4 5	3 9	**3.3**	*2.8*	1 8
Colorintens.	54	65	100	118	143	169	126	Yellow	Dyeppted.

The data in Table I show that the color intensity of the dye increased with the acidity of the solution until approximately *PH* 4.0 was reached and that the dye was precipitated at about *PH* 1.8.

Work on the other factors which, according to Yoe and Hill, influenced the intensity of the lake, showed that the intensity of the color reached a maximum and the dye separated at a slightly higher *PH* in the presence of ammonium acetate. It also showed that the intensity of color increased with increase in temperature or dye concentration.

The Aluminum Lake.—In order to determine the *PH* and quantity of ammonium salts that would produce the maximum color of the lake, a number of solutions were prepared, each of a different *PH* and containing a different amount of ammonium acetate. These were adjusted to *PH* 0.0, 5.0, 4.5 and 4.0 with hydrochloric acid. To 25 cc. of each at room temperature were added **3** cc. of the aluminum solution and 2 cc. of 0.1% dye, both having first been adjusted to the same *PH* as the solution to which they were added. After standing for forty-five minutes for the color to develop they were compared. The relative color intensity was also determined on a check containing 5 cc. of 5 *N* ammonium acetate, 2 cc. of 0.1% dye but no aluminum. The concentrations of ammonium acetate, the *PH* readings and the relative color intensities calculated as in Table **I** are given in Table II.

TABLE II

EFFECT OF VARYING *PH* AND CONCENTRATION OF AMMONIUM ACETATE ON COLOR INTENSITY

		Relative color intensity			
Soln.	**$(NH_4)_2C_2H_3O_2$, cc.**	***PH* 6 0**	**PA 5 0**	**PH 4 6**	***PH* 4.0**
1	Check	8[a]	15"	19"	yellow[b]
2	None	23	55	74	Yellow
3	*2*	24	*64*	75	Yellow
4	5	26	66	77	Lake pptd.
5	7	27	67	76	Lake pptd.

[a] These readings are only approximate. The colors differed from the standard.

[b] These differed so much from the standard that no attempt was made to read them.

The data in Table II show that the color intensity due to the lake and the excess dye which did not enter the lake increased with the acidity of the solution until the point was reached where the lake separated which, in the presence of 5 cc. of 5 *N* ammonium acetate, was at about PH 4.0. Since the color of the dye was only a small part of the total color, the above phenomenon was caused mostly by the lake. The data also show that the intensity of the color increased slightly with the addition of ammonium acetate until about 5 cc. had been added. Therefore this concentration of the salt should be used for making aluminum determinations.

To show the temperature at which maximum color was produced, two solutions, each containing 5 cc. of 5 N ammonium acetate for every 25 cc., were prepared and adjusted to PH 5.0 and 4.5, respectively. Three cc. of the aluminum solution and *2* cc. of the 0.1% dye were added to 25-cc. portions and, after holding the solution at given temperatures for ten minutes, the color intensities were compared. The figures for the PH of the solution, the temperature at which the color was developed and the relative intensities calculated as before are given in Table III.

TABLE III

EFFECT OR VARIATION IN TEMPERATURE ON COLOR INTENSITY

Solution		**1**	**2**	**3**	**4**	**5**	**6**
Temp.. °C.		**27**	**65**	**80**	**85**	**Boil 1 min.**	**Boil 3 min.**
Rel. color intensity	*PH* 5.0	**87**	**107**	**112**	**111**	**112**	**112**
	PH 4.5	**94**	**114**	**120**	**121**	**120**	**121**

Table III shows that under the conditions of the experiment maximum color intensity was obtained when the solution was heated to about 80° for ten minutes or when boiled for one minute.

The effect of the time of standing at room temperature on the development of the color was shown by adjusting a number of solutions to PH 5.0 as in the preceding experiment, developing the colors and comparing their intensities after standing for different lengths of time. The results are shown in Table IV, which gives the relative color intensity expressed in percentage of maximum intensity (obtained by boiling for one minute) corresponding to each different length of time the solution was allowed to stand.

TABLE IV

EFFECT OX VARIATION IN LENGTH OF TIME OF STANDING ON COLOR INTENSITY

Soln.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Temp., °C.	**27**	**27**	**27**	**27**	**27**	**27**	**27**	**Boiling**
Standing, hrs.	**$^1/_6$**	**0.25**	**0.5**	**1**	**1.5**	**18**	**60**	**1 min.**
Col. intens.	**63**	**64**	**66**	**69**	**73**	**90**	**92**	**100**

Table IV indicates that with the given amount of dye and aluminum approximately 64% of the possible maximum color (obtained by boiling for one minute) was developed in fifteen minutes, that it continued to develop at a decreasing rate but that the maximum color obtainable was not reached in sixty hours. Other experiments showed that with a sufficient increase in the dye concentration it was possible to obtain maximum color at room temperature in about twenty-four hours.

From the work done on color development it appeared that maximum intensity of color was obtained when the lake was developed in the presence of 5 cc. of 5 N ammonium acetate in 25-cc. solution at PH 4.5 and allowed to stand for ten minutes at 80° or to boil for one minute.

Decolorization of Excess Dye and Permanency of Lake **Color.**—Since the color of the dye alone in acid solution and that of the lake are quite similar, it was found impracticable to make quantitative determinations of aluminum by comparison of the intensity of the color of the unknown with that of the standard until after the solution was neutralized and the excess dye decolorized. Hence the next step in this work was to try to find optimum conditions for destroying the color of the unused dye while retaining the color of the lake.

The Dye.—In order to determine the PH at which the dye decolorized and the effect of ammonium salts on this PH, several solutions of 25 cc. each were prepared containing salts as shown in Lines 2 and *3* in Table V. Hydrochloric acid to give a *PH* of 4.5 and 2 cc. of 0.1% dye were added to each of these and they were allowed to stand for forty-five minutes for the color to develop. Ammonium carbonate[8] was now added slowly until the color began to fade, after which the addition of small amounts of the carbonate was continued at intervals until the color entirely disappeared. The *PH* was then determined colorimetrically. The results are given in Table V.

TABLE V

EFFECT OF AMMONIUM SALTS ON THE PH AT WHICH DYE DECOLORIZED

Sample	1	*2*	3	4
5 N NH_4Cl, cc.	0	5	0	5
5 N $NH_4C_2H_3O_2$, cc.	0	0	*5*	5
Average PH	8.0	6.9	7.0	7.0

The figures in Table V indicate that the dye was decolorized at a lower *PH* in the presence of ammonium salts and that under these conditions the dye decolorized at *PH* **6.9–7.0.** It should also be stated that the use of a larger quantity of dye or the development of the color at a higher temperature had no effect upon the *PH* at which the color changed.

The Lake.—The maximum *PH* at which the lake color would remain was determined by preparing several solutions containing 5 cc. of 5 *N* ammonium acetate, 2 cc. of 0.1% dye and **0.03** mg. of aluminum and

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[8] Similar results were obtained when dilute ammonium hydroxide or 10% ammonium carbonate in ammonium hydroxide (1–2) was used.

developing the colors as in the preceding experiment. An equal number of similar solutions was prepared but with the dye omitted. The quantity of neutralizing agent necessary to bring each of these latter solutions, respectively, to PH 7.0, 7.1, 7.2, 7.3, 7.4 and 7.5 was carefully determined and these amounts were added to the solutions containing the dye. After standing for thirty minutes for the excess dye to decolorize, the color changes were noted at intervals over a period of two hours and are recorded in Table VI.

TABLE VI

EFFECT OR PH OR SOLUTION ON PERMANENCY OF LAKE COLOR

Sample	**1**	**2**	**3**	**4**	**5**	**6**
PH	*7.0*	*7.1*	**7.2**	*7.3*	*7.4*	*7.5*
Color intens.	Const.	Const.	Const.	**Faded v. sl.**	**Faded sl.**	**Faded rapidly**

Prom Table VI it will be seen that the lake color remained practically constant until after the solution was raised above PH 7.3 and that it decolorized more rapidly as the PH increased above this point. Other experiments showed that the quantity of dye used or the temperature at which the lake was developed had no effect upon this.

Now it seemed important to know whether or not the PH of the solution at which the lake color was developed had any effect on the final color intensity of the lake after the dye had been decolorized. Therefore, a number of solutions were prepared as in the preceding experiment, the lakes developed at PH 5.5, 5.0 and 4.5 and after standing for forty-five minutes the solutions were brought to PH 7.2 with ammonium carbonate. After these neutralized solutions had stood for thirty minutes to allow the excess dye to decolorize, they were compared. The relative color intensities are given in Table VII where *a*, b and *c* under each number represent similar solutions each adjusted to the corresponding PH shown in the table.

TABLE VII

EFFECT OF DEVELOPING THE LAKE AT THREE: DIRFERENT *PH*'S ON THE FINAL INTENSITY OF COLOR

Sample	*la*	*lb*	1*c*	2*a*	2*b*	2*c*	3*a*	3*b*	3*a*
***Pa* of col. dev.**	*5.5*	*5.0*	*4 5*	**5.5**	*5.0*	*4.5*	*5.5*	**5.0**	*4.5*
Rel. final intens.	*90*	*100*	*101*	*115*	*130*	*129*	*90*	*100*	*97*

The results in Table VII show that the lakes developed at PH 4.5–5.0 gave rise to maximum final color intensity.

Other experiments not reported here showed that increasing the amount of dye used in developing the lake increased the color intensity of the final solution and made it possible to increase the concentration of the lake without having it separate. However, the yellow color formed when the excess dye was neutralized gave rise to varying tints which made reading **the colorimeter** very difficult; therefore, the data on this work are omitted.

From the work done thus far it appeared that the maximum final color intensity for practical purposes was obtained when the lake was developed in the presence of 5 cc. of 5 N ammonium acetate at PH 5.0 heated at 80° for ten minutes or boiled for one minute and neutralized to PH 7.1–7.3. It was found that 5 cc. of 1.5 N hydrochloric acid added to the solution gave the desired acidity (PH 5.0). In neutralizing the solution with ammonium hydroxide it was found necessary to use a dilute solution (about 1 N) and add it very slowly with vigorous shaking in order to get concordant results. Apparently a more concentrated solution (5 N) gave rise to localities of momentary high PH where some lake color was destroyed. There appeared to be no advantage in adding the ammonium hydroxide–ammonium carbonate solution which some analysts have used. It was found that 5 *N* ammonium carbonate could be used without loss of color if added slowly (about 5 cc. in 20 sec.) with gentle shaking. Ammonium chloride has a slight buffer effect in the range near PH 7.2 and the addition of 5 cc. of a 5 N solution of this salt before neutralizing made it possible to control more easily the acidity of the solution at this point. Therefore, ammonium chloride and ammonium carbonate were used in the remainder of this work and it was found that 5 cc. of a 3.2 N solution of the carbonate brought the lake to PH 7.2. The formation of carbon dioxide bubbles on the prisms of the colorimeter and occasionally in the bottom of the cups was sometimes quite annoying. This was largely avoided by allowing the cups to stand a few moments after the solution had been poured into them. The presence of bubbles could easily be recognized by the altered color of the solution.

The procedure developed thus far was now used for making a number of determinations on synthetic aluminum solutions. The results of these determinations are given in Table VIII, which also shows the percentage error.

The data in Table VIIIA show that the method gave good results providing the amount of aluminum in the standard was very nearly the same as that in the sample. Otherwise the results were not good, as is more emphatically shown by the determinations in Part B, for which several standards were chosen differing considerably in composition from the samples. These results show that the color intensity is not a linear function of the amount of aluminum present, that when the standards contain more aluminum than the sample the results are high and vice *versa* and that the greater the difference between the amount of aluminum in the standard and the sample, the greater is the error.

Now it appeared safe to assume that if the variable factors in the method (temperature, time, quantity of reagents, etc.) were carefully controlled and if the colorimeter readings of the standard were kept constant, the relation between the colorimeter readings and the amount of aluminum

TABLE VIII

DETERMINATION OF ALUMINUM IN SYNTHETIC SOLUTIONS

	Sample	Aluminum in standard. mg.	Aluminum Present, mg.	Aluminum Found, mg.	Error, %
A	1	0.0300	0.0300	0.0306	+2.0
	2	.0200	.0200	.0200	0.0
	3	.0500	.0500	.0496	−0.8
	4	.0500	.0500	.0480	−4.0
	5	.0400	.0400	.0413	+3.2
	6	.0300	.0320	.0328	+2.5
	7	.0500	.0520	.0516	−0.8
	8	.0400	.0420	.0420	0.0
B	1	.0300	.0050	.0084	+68.0
	2	.0300	.0100	.0151	+51.0
	3	.0300	.0200	.0231	+15.5
	4	.0300	.0300	.0300	0.0
	5	.0300	.0400	.0359	−10.2
	6	.0300	.0500	.0449	−10.2
	7	.0100	.0050	.0067	$34.0
	8	.0100	.0200	.0189	−5.5
	9	.0200	.0100	.0110	$10.0
	10	.0200	.0200	.0197	−1.5

present might be represented by a curve plotted to show this relationship. Furthermore, it should be possible to read directly from this curve the quantity of aluminum present in unknowns.

In order to determine the correctness of this assumption, several series of determinations were made, taking solutions containing 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06 and 0.07 mg. of aluminum for each series and reading each of these against 0.03 mg. of aluminum as the standard. The readings were made with the standard set at 30 or when this was not practical they were calculated to this value. The results are shown in Table IX, which gives the amount of aluminum in the solution, the corresponding colorimeter readings and the averages of these readings.

TABLE IX

COLORIMETER READINGS OP SIX SERIES OP SYNTHETIC ALUMINUM SOLUTIONS

Al, mg.	Colorimeter readings 1	2	3	4	5	6	Av.
0.0050	102.6	106.0	102.6	100.1	..	..	103.1
.0100	58.8	59.5	58.1	54.6	61.5	60.4	58.8
.0200	38.8	39.1	39.3	38.6	40.0	40.0	39.3
.0300	30.0	30.0	30.0	30.0	30.0	30.0	30.0
.0400	24.7	24.2	24.2	24.8	24.4	25.0	24.5
.0500	21.6	21.3	21.1	21.1	21.2	21.1	21.2
.0600	18.3	18.4	..	18.1	18.5	18.9	18.4
.0700	16.9	17.1	..	17.0	16.9	17.0	17.0

Figure 1 shows the relation between the aluminum and average colorimetric readings expressed in Table IX in the form of a graph.

Aluminum determinations were now made on several synthetic solutions by reading the results directly from the curve in Fig. 1. These data are given in Table X, which shows the colorimeter readings, the amount of aluminum present, the amount found and the percentage error.

The values in Table X show that aluminum can be determined colorimetrically by comparing the color intensities of the unknowns with that of one standard and reading the results directly from a curve which shows the relation between the colorimeter reading and the amount of aluminum present. These also show that the method is applicable to solutions containing from 0.0050–0.0700 mg. of aluminum and that the method is accurate to within about 5%. Other determinations which are not recorded here show this to be approximately the limit of error of the method. The result for Solution 7 in Table X indicates that if the curve were continued nearer the zero point for aluminum the method might be useful for solutions containing less than 0.0050 mg. of aluminum. In this case a fair approximation may be made but the color is very faint and if accurate results are desired it is better to make up a standard containing 0.0050 mg. of aluminum and calculate the results.

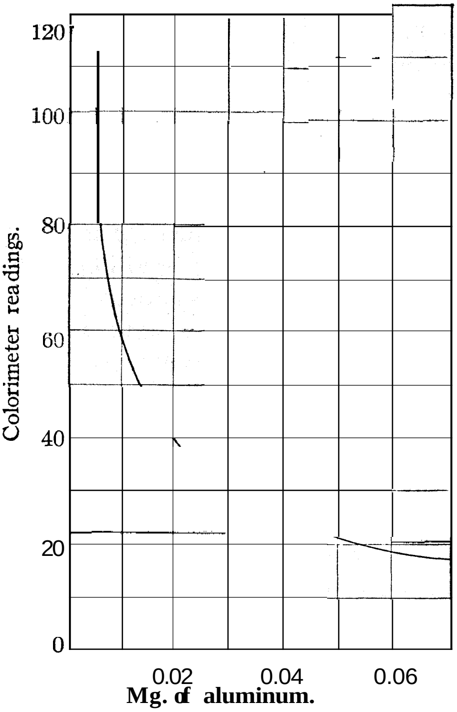

Fig. 1.—Relation between the colorimeter readings and the amount of aluminum.

TABLE X

ALUMINUM DETERMINATIONS READ FROM CURVE IN FIG. 1

Soln.	Colorimeter reading	Aluminum Present, mg.	 Found, mg.	Error, %
1	31.4	0.0280	0.0285	−1.8
2	23.9	.0400	.0410	−5.0
3	20.5	.0530	.0515	−2.8
4	17.2	.0670	.0690	−2.9
5	34.1	.0250	.0250	0.0
6	100.9	.0050	.0052	−4.0
7	176.4	.0030	?	

The Method

The procedure recommended for making aluminum determinations is as follows: transfer the solutions, which should be slightly acid, to 50-cc. volumetric flasks and to each add water to make a volume of about 20 cc.; then add 5 cc. of 5 N ammonium acetate, 5 cc. of 1.5 N hydrochloric acid and 2 cc. of 0.1% dye and place in a water-bath at about 80° for ten minutes. Add 5 cc. of 5 N ammonium chloride, cool to room temperature, add 5 cc. of 3.2 N ammonium carbonate while shaking gently, fill to the mark with distilled water and mix. At this point the reactions should be P_H 7.1–7.3 and the red color of a blank should disappear in about fifteen minutes. (The exact concentration of the reagents is not important, but the final P_H is, and the amount of ammonium carbonate necessary to bring the solution to the above P_H should be determined by neutralizing similar solutions without adding the dye.) Simultaneously with the above, run a standard (or standards if necessary) containing a given quantity of aluminum. After standing for twenty minutes for the excess dye to decolorize, compare the color intensities and read the amount of aluminum from a curve plotted as described in the following paragraph.

When only a small number of determinations are to be made, prepare four standards containing 0.0100, 0.0300, 0.0500 and 0.0700 mg. of aluminum, respectively, and run these with the samples. Compare all of these solutions with the standard containing 0.0300 mg. of aluminum and calculate the results to a colorimeter reading of 30 for this standard. Arbitrarily give 0.0050 mg. of aluminum a reading of 100 and with this and the four readings on the standards plot a curve similar to Fig. 1. Read the quantity of aluminum in each sample from this curve. If a large number of determinations are to be made extending over a period of time, it is advisable to make determinations on several series of standards and plot a curve from the average of these results, as was done in obtaining the curve in Fig. 1. Having done this it is necessary to run only one standard each time determinations are to be made and read the results from the curve.

Summary and Conclusions

1. The colorimetric method in which aurintricarboxylic acid is used for determining aluminum has been modified so that samples ranging from 0.0050 to 0.0700 mg. of aluminum may be compared with one standard and the amount of aluminum in each sample may be read directly from a curve. The results are accurate to within about 5%.

2. Maximum color intensity was obtained in the presence of 10% of 6 N ammonium acetate when the solution was at approximately P_H 4.0 and held at a minimum temperature of 80° for about ten minutes.

3. In the presence of 5 cc. each of 5 N ammonium acetate and ammonium chloride the dye changed color at about P_H 7.0. A neutral or

alkaline solution of 2 cc. of 0.1% dye in a volume of 50 cc. was very nearly colorless.

4. The lake color remained sufficiently permanent for making determinations until the solution was raised to PH 7.4.

5. The presence of ammonium acetate and chloride as buffers was found advantageous for controlling the PH of the solution.

6. Ammonium carbonate was found more suitable for decolorizing the excess dye than either ammonium hydroxide or a solution of ammonium carbonate in ammonium hydroxide.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. IX. URANYL SULFATE AS SENSITIZER FOR THE PHOTOCHEMICAL DECOMPOSITION OF OXALIC AND MALONIC ACIDS

BY WILLIS CONWAY PIERCE

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The photochemical decomposition of malonic acid, both in the presence and absence of uranyl salts, has been the subject of a previous study,[1] while the decomposition of oxalic acid has been repeatedly investigated.[2] The results indicate that the mechanisms of the sensitized decompositions of the two acids may be different and the present work was undertaken in order to obtain a more thorough comparison between the two.

I. Temperature Coefficient

There is some discrepancy in the values given for the quantum efficiency of the oxalic acid decomposition but the generally accepted value seems to be one.[3,4] Various workers have reported a temperature coefficient of unity. The quantum efficiency for the decomposition of 0.05 M malonic acid with 0.0025 M uranyl sulfate was found[1] to be about 0.25, and to be in some degree at least independent of wave length. Buchi[3] attributed the effect of uranyl sulfate to complex formation in the case of oxalic acid. Müller,[5] on the other hand, has attributed the effect to collisions of the second kind between activated uranyl ions and oxalic acid molecules or oxalate ions. A somewhat similar explanation was suggested[1] for the

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[1] See Pierce, Leviton and Noyes, THIS JOURNAL, 51, 80 (1929), for more complete references.

[2] See Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, 1928, for a review of this work.

[3] Biichi, *Z. physik. Chem.*, 111,269 (1924).

[4] Bowen and Watts, *J. Chem. Soc.*, 127, 1607 (1925).

[5] Müller, *Proc. Roy. Soc. London*, 121A, 313 (1929).

uranyl sulfate–malonic acid reaction, although it was said that complex formation was not definitely ruled out.

It seemed that the temperature coefficient might furnish evidence as to the applicability of the two explanations and this was determined for uranyl sulfate with malonic acid and uranyl sulfate with oxalic acid. A value of one was found for the oxalic acid, confirming the results of Bruner and Kozak[6] and Bacon.[7] The sensitized decomposition of malonic acid showed a temperature coefficient of 1.13 ± 0.02 between 3 and 73°.

Experimental

A quartz mercury arc lamp was mounted vertically and two quartz water jackets surrounding quartz test-tubes were placed parallel to the lamp at a distance of two centimeters. The solutions were placed in the test-tubes and were kept at the desired temperature by a rapid flow of water through the jackets. The system was tested for uniformity by exposing similar samples of a uranyl sulfate–oxalic acid solution in the two vessels and measuring the decomposition by titration with permanganate. Malonic acid solutions were analyzed by titration with carbonate-free sodium hydroxide solution with phenolphthalein indicator. Results are given in Table I.

TABLE I

TEMPERATURE COEFFICIENT.[a] $KMnO_4$, 0.105 N. NaOH, 0 05 N

Substances	Temp. interval, °C.	Decomposition cc. $KMnO_4$ hot	cold	Ratio of rate hot/cold	Temp. coef.
10 cc. 0.2 M $H_2C_2O_4$; 0.002 *M* UO_2SO_4	3–63	9.94	8.55	1.08	1.01+
	3-63	10.73	10.98	0.98	1.00
		NaOH, cc.			
	3–73	11.55	5.00	2.31	1.13–
10 cc. 0.1 M $H_2C_3H_2O_4$; 0.0025 M UO_2SO_4	3–73	11.25	4.70	2.39	1.13+
	3–73	13.60	5.74	2.37	1 13
	3–53	11.10	5.20	1.95	1.14+

[a] By "temperature coefficient" is meant the ratio of the rates. $R_{t+10°}/R_t$.

These results confirm a large number of previous runs in which but a single sample was exposed.

II. Absorption Spectra

The absorption coefficients of uranyl salts are greatly enhanced by the presence of organic acids. Henri and Landau[8] first described this for oxalic acid and uranyl sulfate and their work was cited by Büchi as evidence for complex formation. It was stated in the previous paper that no such effect was found with malonic acid, but a further investigation at higher

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[6] Bruner and Kozak, *Z. Elektrochem.*, 17,355 (1911).

[7] Bacon, *The Philip.* **J.** *of Sci.*, 5,281 (1910).

[8] Henri and Landau, *Compt. rend.*, **158**, 181 (1913).

frequencies (using more dilute solutions) showed that in the range 220 mμ to 320 mμ the absorption coefficients are increased by the presence of malonic acid. The effect is not so marked at longer wave lengths. Ghosh and Mitra[9] assumed that this enhancing effect is due to the formation of a complex between the uranyl salt and the organic acid and used the absorption coefficients to calculate the degree of formation. Both oxalic and malonic acids were investigated by them. They based their calculations on the assumptions that (1) one molecule of the organic acid unites with one molecule of the uranyl salt to form a molecular complex, (2) the mass law applies to this combination and (3) the complex molecule has a definite absorption coefficient for each wave length. They found the equilibrium constants

$$\left(K = \frac{[\text{complex}]}{[\text{uranyl salt}]\,[\text{organic acid}]}\right)$$

K = 115 for oxalic acid–uranyl sulfate complex and K = 80 for malonic acid–uranyl sulfate complex. According to these values oxalic and malonic acids form complexes of about the same degree of stability but the absorption of the oxalic acid complex is much greater than that of the malonic acid complex.[10]

The work of Müller,[5] Jette and West,[11] and West, Müller and Jette[12] suggested that the increase in the absorption might be due to quenching the fluorescence of the uranyl ion. They found that chloride ion was effective in quenching the fluorescence and that sulfate ion had relatively little effect. The absorption coefficients were determined for uranyl sulfate with these added ions. Neither had an appreciable effect in dilute solution but 0.001 M uranyl sulfate in saturated potassium chloride or potassium sulfate showed practically the same absorption coefficients as when dissolved in 0.01 M oxalic acid. From these results and the fact that Beer's law is obeyed for dilute solutions of uranyl salts it was concluded that the quenching of the fluorescence is probably not the reason for the enhancing of the absorption. The peculiar enhancing by saturated salt solutions may be due to the formation of very unstable complexes but no attempt was made to investigate these.

III. Effect of Concentration on the Rate of Reaction

(a) Uranyl Sulfate.—It was stated in the previous paper that the rate of reaction varied with the concentration of uranyl sulfate when it was

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[9] Ghosh and Mitra, *J. Indian Chem. Soc.*, *4*, **353** (1927).

[10] Absorption coefficients were determined for oxalic and malonic acids and for their solutions with uranyl sulfate before noting the above work. The results were in qualitative agreement with the work of Ghosh, although the difference in the enhancing due to oxalic and malonic acids was not so great as that found by Ghosh.

[11] Jette and West, *Proc. Roy. Soc. London*, **121A,** *300* (1928).

[12] West, Muller and Jette, *ibid.*, **121A,** *294* (1928).

less than 0.0025 M and was independent of concentration in the range 0.0025 to 0.01 M. This was for reactions carried out in vessels exposing a layer of solution one to two centimeters in depth. All of the previous work was done with only one exposure at a time and was open to error in accidental variation in the light intensity. A new series of experiments was carried out with all the samples of varying concentration lighted simultaneously on a rotating motor-driven turntable. The results are listed in Table II. They are in agreement with the previous results.

TABLE II

VARIATION OF RATE WITH CONCENTRATION OF URANYL SULFATE

10-cc. samples lighted in open porcelain crucibles. Depth of liquid, 1.5 cm. Malonic acid, 0.05 M. NaOH, 0.0528 *N*.

Concn. UO_2SO_4	Amt. decomp. (cc. NaOH) I	II	Relative rate 2.72 = 1	8.15 = 1
0.0000	0.50	1.71	0 18	0.21
.0005	1.75	5.05	0 64	0 62
.0010	2.29	6.03	0 84	0.74
.0015	2.38	6.76	0 88	0 83
.0025	2.75	7.58	1 01	0.93
.0050	2.63	8.39	0 97	1 03
.0075	2.86	8.47	1 05	1 04
.0100	2.64	8.15	0.97	1 00

(b) Malonic Acid.—It has previously been shown that with 0.01 M uranyl sulfate the rate varied with the concentration of malonic acid. The effect is most marked at small concentrations of acid. The importance of this led to a reinvestigation, using a greater variety of mixtures. All samples were lighted simultaneously on the rotating apparatus, thus eliminating errors due to fluctuations in the light intensity. The total reaction had to be kept small in order to prevent complete decomposition of the samples having small amounts of malonic acid, and on this account the experimental error was quite large. Averages taken from a large number of determinations gave sufficient accuracy to determine the trend of the rate curve. Results of two typical runs are given in Table III.

TABLE III

VARIATION IN RATE WITH CONCENTRATION OF MALONIC ACID

Uranyl sulfate, 0.0116 M. 20-cc. samples used. NaOH, 0.0528 N

	2 5-Hour run				5.8-Hour run			
Init. concn. malonic acid	0.0048	0.0092	0.023	0.040	0.0092	0.023	0.046	0.092
Molar ratio = x	0.4	0.8	2.0	4.0	0.8	2.0	4.0	8.0
Amt. dec., cc. of NaOH	1.30	1.59	1.95	2.60	2.97	4.91	5.58	6.18
Rel. rate, x = 8, for unity	0.45	0.55	0.67	0.90	0.48	0.79	0.90	1.00
Av. molar ratio, $\bar{x}$	0.25	0.61	1.8	4.0−	0 4	1.5	4.0−	8.0−

The two series of runs were calculated to the same relative rate of unity for samples having a molar ratio of 8. Since the concentration changed during a run, an average value of x (molar ratio) was calculated and used as the effective molar ratio. This does not accurately represent the effective concentrations during a decomposition but it may be taken as a first approximation.

IV. Discussion of Results

Some points of difference are noted in the catalyzed decompositions of oxalic and malonic acids. For example, the temperature coefficient of the former is one while that of the latter is 1.13. The quantum efficiency of the former is given as one, but for the latter a value of about 0.25 was found. On the other hand, many points of similarity lead to the conclusion that the function of the uranyl sulfate is the same in both cases. It seems that both reactions may be satisfactorily explained by the assumptions of Biichi that a light-sensitive complex is formed by the uranyl ion and the organic acid, and that decomposition is caused only by the light absorbed by this complex. There is, however, some evidence for the alternative theory that the uranyl ion transfers energy to the acid molecule by collisions of the second kind. Indications of complex formation to be found are: (1) The conductivity of uranyl salts was shown by Dittrich[13] to be lowered by the addition of sodium oxalate.

(2) The quantitative work of Ghosh and Mitra on the absorption spectra seems to point to complex formation.

(3) The variation in rate with the concentration of acid may be in agreement with the "complex" theory. Büchi showed that for oxalic acid the rate is nearly constant when the molar ratio is greater than one (acid in excess). This is difficult to explain by collisions of the second kind unless the activated uranyl ions have a very long life and may be deactivated only by collision with oxalic acid molecules. It is, however, in harmony with the "complex" theory if the complex has such large absorption coefficients that practically all of the effective light is absorbed by it, and if the complex is so stable that when a molar ratio of unity is reached practically all of the uranyl ions are combined. Both of these assumptions are necessary to account for a quantum yield of unity, as found by Biichi.

These assumptions, however, are not in agreement with the values of Ghosh[8] for the stability of the complex and its absorptive power. Buchi used 0.0167 M uranyl sulfate solutions with equimolar oxalic acid. Ghosh found an equilibrium constant of 80 for this reaction. This value leads to a calculated concentration of complex of 0.006 M for the above solution. The relative absorption for a given frequency is given by the relation

$$\text{Fraction of light absorbed by complex} = \frac{k_1c_1}{k_1c_1 + k_2c_2}$$

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[13] Dittrich, *Z. physik. Chem.*, **29**, **449** (1899).

where k_1 and k_2 are absorption coefficients of complex and uranyl ion, respectively, and c_1 and c_2 are their concentrations. In order for the complex to absorb most of the light its absorption coefficient must be very much greater than those of the uranyl ion if the relative concentrations are as given by the calculation. It seems then that (1) the complex may be more stable than postulated by Ghosh, (2) it may have larger absorption coefficients, or **(3)** energy absorbed by the uranyl ions may be transferred to the complex by collisions of the second kind of very high efficiency.

The case of malonic acid is much the same. The increase in rate beyond a molar ratio of 1 is very much less than when the uranyl sulfate is in excess. The reaction may be satisfactorily interpreted as due to the absorption of light by the complex and decomposition of the activated complex. The steady rise in rate with increasing acid concentration may be due to the formation of more of the complex, thus increasing the fraction of the light absorbed by the complex.

This interpretation does not conflict with the observation that in 0.05 M malonic acid solutions the rate is independent of the uranyl salt concentration in the range 0.0025 to 0.01 M. At such concentrations absorption of the effective light is undoubtedly nearly complete even in very shallow layers, and increase in the complex concentration should not cause an increase in rate. Further, increase in the concentration of uranyl ion decreases the molar ratio so that the fraction of the uranyl ion converted to complex becomes smaller as its total concentration is increased, and less of the light is available for the reaction. A calculation of the fraction converted may be made using the equilibrium constant of 115 as determined by Ghosh. At initial concentrations of $UO_2SO_4 = 0.0025$ and malonic acid $= 0.05$ M the concentration of complex is 0.00217 M, or 86.7% of the ion has reacted. For 0.01 M UO_2SO_4 and 0.05 *M* malonic acid the complex concentration is 0.00827 M, corresponding to 82.7% reaction. Since the absorption coefficients of the complex are higher than those of the uranyl ion, the fraction of the light absorbed by the complex does not change greatly over this range of concentration of uranyl ion.

(4) The temperature coefficient of unity may be in harmony with either mechanism for oxalic acid. If the reaction is a zero order decomposition of a complex, it appears that the activation of any molecule may lead to decomposition, and that thermal activation is not necessary. It would seem that temperature changes have little effect on the stability of the complex since the reaction rate is independent of temperature. If, on the other hand, the reaction is brought about by collisions of the second kind, all absorbed quanta must be utilized in activating oxalic acid molecules and rise in temperature should cause no change in rate.

It is significant that the temperature coefficient of the malonic acid reaction is so much larger, but this fact as well as the quantum efficiency may agree equally well with either explanation.

Collisions of the second kind do not seem to offer an adequate explanation of the enhancing of absorption when organic acids are added to uranyl sulfate solution. On the other hand, complex formation does not seem to explain the observation of Müller[5] that addition of certain ions to a uranyl sulfate–oxalic acid solution lowers the rate of reaction. He found that the order of effectiveness of chloride, bromide and thiocyanate ions is the same as their order of effectiveness in quenching the fluorescence of uranyl ions. Both effects are ascribed to the ability of the added ions to deactivate the uranyl ions on collision. If such a deactivation occurs, the effectiveness of added ions in reducing the rate of oxalic acid decomposition should depend (a) on the effectiveness of transfer of energy from the uranyl ion to retarder and to reactant, and (b) the relative number of collisions of each with the activated uranyl ions. These assumptions have been used to calculate the rate of decomposition of 0.1 M oxalic acid in the presence of various retarders. The experimental results are those given by Müller.[5] Results are summarized in Table IV. The assumed effectiveness of the deactivation per collision with a retarding ion is: chloride ion, **0.228;** bromide ion, **0.5;** thiocyanate ion, **1.0.** It is significant that the inhibitor having the greatest effect has an efficiency of deactivation of unity.

Table IV

Inhibiting Effect of Added Ions

Concn. of added ion	Calcd. rate Cl	Obs. rate Cl	Calcd. rate Br	Obs. rate Br	Calcd. rate SCN	Obs. rate SCN
0.02	26.9	27.1	25.6	26.2	23.3	23.0
.05	25.8	26.1	23.3	24.2	18.7	18.5
.10	(24.8)	24.8	21.0	22.3	14.0	13.8
.20	23.7	24.2	18.7	19.4	9.3	8.6

The excellent agreement obtained lends support to this theory.

Each theory then may account for many of the observed facts, and it seems that further work is needed in order to establish either one. A third possibility is that the reaction is brought about by both complex formation and collisions of the second kind.

V. Summary

1. The temperature coefficient is **1.13 ± 0.02** for the photolysis of malonic acid in presence of uranyl sulfate. It is unity for oxalic acid–uranyl sulfate, as reported by previous workers.

2. The rate of the reaction varies with the concentration of uranyl sulfate and approaches a constant value. The rate varies with the concentration of malonic acid. This effect is greatest when the molar ratio of malonic acid to uranyl sulfate is less than unity. At ratios greater than unity the change in rate with concentration is small.

3. The oxalic and malonic acid reactions seem to be similar although they show a marked difference in their temperature coefficients and quantum efficiencies.

4. Two mechanisms are discussed. The reaction may be due to the decomposition of an intermediate uranyl ion–acid complex, or it may be explained by collisions of the second kind between activated uranyl ions and acid molecules.

CHICAGO, ILLINOIS

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

THE HEAT CAPACITY OF TOLUENE FROM 14°K. TO 298°K. THE ENTROPY AND THE FREE ENERGY OF FORMATION

BY KENNETH K. KELLEY[1]

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Very few low temperature thermal measurements on aromatic hydrocarbons have been made. The only true specific heats which have been published are those of Nernst[2] for benzene but even these data are very scanty and do not agree well among themselves.

This paper presents specific heat, heat of fusion and temperature of fusion data for toluene. The specific heat measurements were carried down to 14°K. The methods and apparatus and the accuracy of measurement have been discussed elsewhere.[3]

One change in the apparatus was made before starting this work. Due to an unfortunate explosion the portable hydrogen liquefier, previously used, was demolished. A new liquefier, similar to that described by Latimer and Greensfelder,[4] was built in as a permanent unit. Both of these liquefiers were designed by Mr. G. F. Nelson of this Laboratory and built under his supervision.

Material.—The toluene was the best product of the Eastman Kodak Company (sulfur free). Treatment of a sample with concd. sulfuric acid gave no coloration in ten minutes. The material was dried for several days with fused calcium chloride, decanted off, and carefully fractionated three times. The middle portion used had a volume of 200 cc. and a boiling range of 0.03". The density, d_4^0, 0.88456, compares favorably with the Leiden measurement: d_4^0, 0.88445, and with that of Biron,[6] d_4^0, 0.88450. The fusion curves indicated exceptional purity.

The Measurements.—The specific heat results are given in Table I and shown graphically in Figure 1. No abnormal behavior was noted in either the crystals or liquid.

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[1] National Research Fellow in Chemistry.

[2] Nernst, *Ann. Physik*, (4) *36*, 395 (1911).

[3] Kelley, THIS JOURNAL, 51, 180 (1929).

[4] Latimer and Greensfelder, *ibid.*, 50,2209 (1928).

[5] *Comm. Phys. Lab. Univ. Leiden,* No. 157.

[6] Biron, *Chem. Zentr., I,* 1910 (1913).

TABLE I

SPECIFIC HEAT OF TOLUENE (IN 15°-GRAM CALORIES)

T, °K.	C_p, cal./mole	T, °K.	C_p, cal /mole	T, °K.	C_p, cal./mole
		Crystals			
16.72	2.202	50.86	1033	120.45	16.39
20.50	3 298	60.48	11.73	128.52	17.16
23.97	4.268	69.16	1264	135.77	17.53
27.74	5 346	75.23	13.19	144.07	17.94
32.31	6 532	8444	13.89	152.41	18.46
37.22	7.776	93.29	14.29	162 34	19.29
41.68	8 676	102.73	15.00	166.60	19.24
45.80	9 483	112 25	15 80		
		Liquid			
183.83	3202	222.77	33.41	262 76	34 67
192.60	32.38	232 68	33.50	273.17	35.37
203.05	32.58	242.52	33.64	284.44	36.59
213 23	32 74	252.48	34.57		

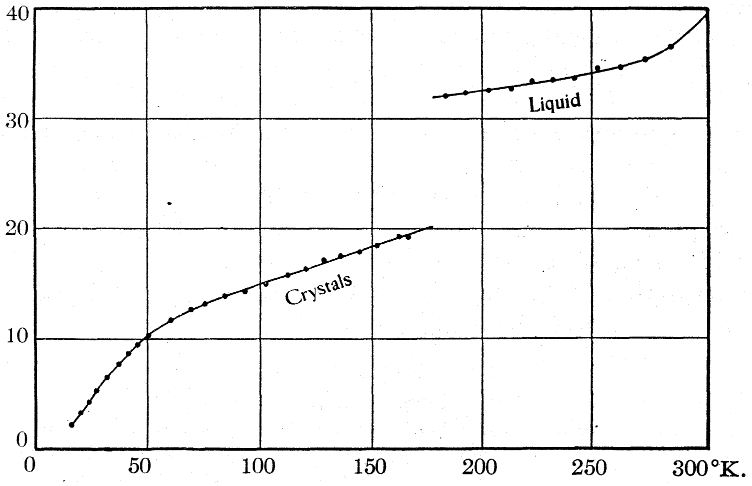

Fig. 1.—The heat capacity of toluene in calories per mole.

The heat of fusion and temperature of fusion data appear in Table II. The fusion temperature of toluene recorded here is almost exactly (to 0.01°) the same as that obtained at Leiden.[5]

TABLE II

FUSION DATA

T, °K.	Heat of fusion in cal per mole 1st result	 2nd result	Mean
177.95	1584	1579	1582

The Entropy.—The entropy was calculated in the usual manner. The extrapolation below the initial temperature of the lowest measurement was made by means of the Debye function with $\Theta = 91$. Table III contains the results of the entropy calculation.

TABLE III

ENTROPY OF TOLUENE

0–14 °K. (extrap.)	crystals	= 0.52
14–177.95	crystals	= 25.50
1582/177.95	fusion	= 8.89
177.95–298.1	liquid	= 17.46
$S_{298.1}$ for 1 mole of liquid toluene =		52.4 ± 0.3 E. U.

Preliminary Measurements on *m*-Xylene.—Similar measurements were carried out on m-xylene. However, the fusion curves revealed a considerable amount of impurity and for that reason the specific heat data are not worthy of publication. The entropy value obtained, namely 60.3 E. U. per mole, is probably not in serious error and has been checked by Parks and Huffman,[7] who also unfortunately did not have a pure sample.

Free Energy Calculations and Discussion.—The free energy of formation from the elements was calculated by means of the equation, $\Delta F = \Delta H - T\Delta S$. The heat of combustion data of Richards and co-workers[8] were used, corrections being made to 15° calories and to the standard of temperature used here, 298.1 °K. The heats of formation of carbon dioxide and water and the values for the entropies of the elements were those adopted in previous work.[3] For the purpose of comparison the free energy of benzene has also been calculated, using the value of 42.4 E. U. for its entropy at 298.1 °K.[9] Table IV contains the resulting thermal data, the 15° calorie being used throughout.

TABLE IV

THERMAL DATA

Substance	Heat of combustion	$\Delta H_{298.1}$	$\Delta S_{298.1}$	$\Delta F_{298.1}$
Benzene	781,700	11,120	−54.2	27,300
Toluene	935,100	1,930	−75.1	24,300
m-Xylene	1,090,500	−5,260	−98.1	24,000

From the entropy of benzene and the values given for toluene and m-xylene in this paper it may be seen that the entropy difference between benzene and toluene is 10.0 units and between toluene and m-xylene 7.9 units. These differences are of the same order of magnitude as the value associated with a CH_2 increment in the homologous series of primary

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[7] Parks and Huffman, personal communication.

[8] Richards and Barry, THIS JOURNAL, 37, 993 (1915); Richards and Davis, *ibid.*, 42, 1599 (1920).

[9] This value was obtained by Parks and Huffman of Stanford University from their unpublished measurements. From Nernst's data a value of 42.2 E. U. may be calculated.

saturated aliphatic alcohols,[10] which has been shown to be 7.7 E. U. In the case of the alcohol series the free energy of formation changed by about 500 cal. per CH_2 group added. No similar definite statement can be made in the present case partly because the heats of combustion utilized in spite of their high percentage accuracy may be in error by a few hundred calories due to their magnitude.

Summary

1. Specific heat measurements on toluene covering the temperature range from 14 to 298°K. have been made.
2. The heat of fusion and temperature of fusion were measured.
3. The entropy and free energy of toluene at 298°K. have been calculated. Preliminary values on m-xylene are also included.

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[CONTRIBUTION NO. 16 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

THE MOVEMENT OF GASES AROUND ELECTRICALLY HEATED WIRES

BY SAM LENHER AND GUY B. TAYLOR

RECEIVED MAY 11, 1929 PUBLISHED SEPTEMBER 5, 1929

In conducting some experiments on the kinetics of the catalytic oxidation of sulfur dioxide by the hot wire method in which the pressure change was being followed on a mercury manometer, it was observed that the mercury meniscus oscillated slightly, indicating a periodic pressure change. Further investigation showed that this periodic effect was not a catalytic phenomenon since it occurred in air and other gases where no chemical reaction was possible.

Platinum wires, 0.25 mm. in diameter and 10 cm. or more in length, were sealed in glass cylinders 3 to 6 cm. in diameter. When the wire was heated electrically to any temperature from about 300° to a white heat, a small periodic pressure change could be detected on a sensitive manometer. The fluctuations occurred from 50 to 100 times per minute and were synchronized with a minute change in the heating current. The current fluctuation was detected by putting the secondary of a small transformer in series with the storage battery used for heating the wire and connecting the primary with a high sensitivity galvanometer. The same effects were observed with wires sealed in spherical glass vessels.

The magnitude of the pressure change at a pressure of one atmosphere when the wire was either nearly vertical or horizontal was a fraction of a centimeter of water. As the tilt of the vessel was increased the periodic

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[10] Kelley, THIS JOURNAL, 51, 779 (1929).

fluctuation became more pronounced, until at a tilt angle of 45° the change became several centimeters of water.

The periodic pressure change was observed with a nearly horizontal wire in air, nitrogen, argon and carbon dioxide but not in hydrogen or helium. The effect, with air, decreased with decrease of pressure from two atmospheres to one-quarter atmosphere, where in this particular experiment the periodic phenomenon stopped.

It appeared probable that the periodic phenomena were connected with convection currents in the gas; this was confirmed by experiment. A platinum wire was sealed vertically in a cylindrical glass vessel with a tungsten weight on the lower end dipping into mercury. The vessel was immersed in a large water thermostat and a gas along with a thin mist of sulfuric acid or titanium hydroxide was introduced. The white mist made the movements in the gas due to convection actually visible. The vessel was illuminated from the side by light from a Pointolite lamp. When the wire was heated electrically a zone was observed around the wire which was free from mist in sharp contrast to the body of gas. This zone appears to be the conduction zone postulated by Langmuir[1] and others.[2]

Langmuir, in studying the energy losses from hot wires, assumed that the transfer of heat from a hot body to a gas in contact with it took place across a thin film of gas next to the heated body through which heat was transferred principally by conduction and radiation. The mist-free zone

TABLE I

DIAMETER OF MIST-FREE ZONE AROUND A HOT PLATINUM WIRE (WIRE DIAMETER, 0.25 MM.)

E/I	Zone diam, mm.	Press., mm.	*E/I*	Zone diam, mm	Press., mm.	Gas	*E/I*	Zone diam, mm.	Press., mm.
Air—Sulfuric Acid Mist			Helium—Titanium Hydroxide Mist			Titanium Hydroxide Mist			
1.8	5	760	1.1	4	760	Air	1.9	5	760
2.0	6	760	1 2	4	760	Air	2.0	6	350
2.3	6	760	1.3	5	760	Air	2 0	7–9	300
2.4	[a]	760	1.4	6	760	Air	2.0	[b]	200
2.0	6	340	1.5	7	760	Hp	2.0	10	760
2.0	10+	290	1.6	8	760	Hp	1.1	4	760
2.0	[b]	170	1.8	9	760	Air	1 3	3	760
			1.9	10	760	Air	1.8–2.0	5	760
			2 0	10	760	Air	2 3	6	760
						Air	2 5	[a]	760

[a] Zone broken up by convection currents. [b] Zone too wide to be measured.

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[1] Langmuir, *Phys. Rev.*, 34, 401 (1912); *Trans. Am. Inst. Elec. Eng.*, 31, 1011 (1912); *Trans. Am. Electrochem. Soc.*, 23,299 (1913).

[2] For the early literature on the conduction zone theory of convection *see* Dalby, *Proc. Inst. Mech. Eng. (London)*, 921 October (1909).

observed in the present experiments followed the behavior of the conduction zone postulated by Langmuir in all respects except one important one. As Langmuir observed, the diameter of the zone was greater in hydrogen and helium than for air at the same wire temperature. Its diameter increased with decrease in pressure as observed with the conduction zone by **Kennelly.**[1,3]

However, the zone observed here was not independent of the wire temperature. This is shown clearly by the data in Table I giving the relation of the diameter of the zone to the wire temperature and the gas pressure for several gases. Resistance of the wire measured as E/I was used as a criterion of equal temperature in the gases. At the high resistances the wire was white hot and at the lower resistances it was not visibly red. The dependence of the zone diameter on the wire temperature was also demonstrated under conditions where the body of the gas was not appreciably heated by the hot wire. A platinum wire was placed vertically in a large glass vessel containing a dilute titanium hydroxide mist in air. The air 1 cm. away from the glowing wire was only 10° above room temperature, but the increase in the diameter of the mist-free zone with increase of wire temperature was the same as that given in the experiments summarized in Table I.

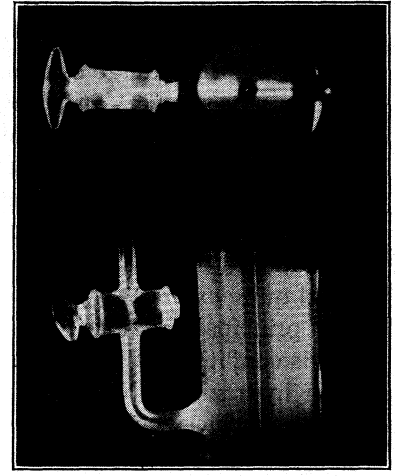

Fig. 1.

In hydrogen and helium the convection currents in the body of the gas outside the zone around the wire were streamline in character while in the other gases the currents tended to become turbulent, periodic and to break into the zone. The periodic pressure change synchronized with a clearly marked visible periodic turbulence in the convection currents.

Figure 1 shows the mist-free zone around a hot wire viewed from the side and from above through a plane window.

Summary

1. A periodic pressure change has been observed in vessels containing an axially placed electrically heated wire. The periodic pressure change has been found to be synchronized with a corresponding fluctuation in the heating current.
2. A mist-free zone around a hot wire in a gas containing a dilute mist

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[3] Kennelly, *Trans. Am. Inst. Elec. Eng.*, *28*, 363 (1909).

has been noted. It has been shown that this zone behaves like the conduction film assumed to exist around a heated body.

3. It has been shown that the diameter of the mist-free zone is dependent on the wire temperature.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

STUDIES ON HYDRAZINE. THE AUTO-OXIDATION

BY E. C. GILBERT

RECEIVED MAY 11, 1929 PUBLISHED SEPTEMBER 5, 1929

The strength of dilute solutions of hydrazine hydrate decreases rapidly in the presence of air. It has been shown[1] that this is due to oxidation by atmospheric oxygen. The reaction between oxygen and hydrazine has been studied also by Browne and Shetterly[2] who passed oxygen and ozone through hot hydrazine solutions, acid, neutral and alkaline. They found no products except nitrogen and in one case a trace of hydronitric acid. The oxidation of hydrazine in the presence of platinum black has been studied quite extensively[3] but this procedure as will be shown removes one of the principal products of the reaction. It is possible, though the evidence is conflicting, that platinum black also effects a catalytic decomposition of hydrazine. None was able to find a mathematical expression for the rate at which the hydrazine is oxidized.

The present work represents a study of the rate of oxidation of hydrazine hydrate in dilute solution by pure oxygen and by air. One of the most interesting developments was the discovery that considerable quantities of hydrogen peroxide are formed in the reaction. This is, of course, a concomitant of many auto-oxidations but hydrazine is a very powerful reducing agent and under some conditions at least reacts readily with peroxide. The presence of peroxide is of particular interest because it interferes seriously with many methods of determining hydrazine. In addition to this the velocity of oxidation under the conditions adopted has been found to follow a simple mathematical expression over a wide range of concentration, temperature and alkalinity.

Experimental Part

(1) **Procedure.**—The apparatus consists of an inverted Erlenmeyer flask into the mouth of which is fitted, by a ground joint, a Jena Gooch crucible containing a medium porous fritted glass disk through which oxygen may be passed into the solution. A hole made in what was formerly the bottom of the flask serves for the introduction of the

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[1] Bray and Cuy, THIS JOURNAL, 46, 1786 (1924).

[2] Browne and Shetterly, *ibid.*, 31, 790 (1909).

[3] Tanatar, *Z. physik. Chem.*, 40, 475 (1902); 41, 37 (1902); Purgotti and Zanichelli, *Gazz. chim. ital.*, 34, I, 57 (1904); Gutbier and Neundlinger, *Z. physik. Chem.*, 84, 203 (1913).

stirrer and for the withdrawal of samples. The reactions are carried out at constant temperature. For the work described here, the interior of the flask was coated with paraffin, as was also the stirrer. The solution was stirred at a constant rate just sufficient to ensure uniformity of concentration; too rapid stirring drew the bubbles of oxygen into the stirrer. In some runs stirring was omitted for periods of thirty minutes at a time with no noticeable effect. It was, however, necessary at the start, Oxygen passed through at the rate of five liters per hour as measured by a calibrated flowmeter. Some runs were made at 6.5 liters per hour but no difference was found. Too rapid flow of gas causes an unduly large loss of hydrazine by volatilization

At the beginning of a run, water and sodium hydroxide (total volume 100 cc.) were introduced into the reacting vessel and saturated with oxygen. The proper amount of hydrazine hydrate (Eastman Kodak Company 50% solution) was added and after one minute a sample (2 cc.) was withdrawn for analysis. At further intervals of five minutes or more samples were withdrawn alternately for the determination of hydrazine and peroxide. Hydrazine was determined by the iodic acid method.[4] Peroxide interferes seriously with this method and must be removed. Both hydrazine and peroxide are reducing agents but peroxide is also an oxidizing agent so the following procedure was adopted, after trial. The sample of hydrazine containing peroxide is run into 6 N sulfuric acid and a few drops of sulfurous acid added. The peroxide is destroyed and so far as could be detected under these conditions the hydrazine is unaffected, The solution was boiled for five to ten minutes to remove excess sulfur dioxide and the hydrazine determined as usual. A test (containing no peroxide, however) went as follows:

Sample of hydrazine sulfate, *cc.*	H_2SO_3, *cc.*	HIO_3, *cc.*	$Na_2S_2O_3$, *cc.*
2.00	1.0	10.00	5.45
2.00	0.0	10.00	5.45

Peroxide could always be detected if present since the final starch–iodine end-point is not permanent if peroxide is present. Peroxide was determined as follows, though no great precision can be claimed for the method. The sample (2 cc.) was run into 3 cc of 6 *N* sulfuric acid in a glass-stoppered flask and carbon dioxide passed through for at least five minutes to remove oxygen from the solution and flask. Potassium iodide was added and after standing for ten to fifteen minutes the liberated iodine was titrated with 0.005 N thiosulfate. In the presence of acid of this concentration hydrazine should react so slowly with iodine that the error would be negligible. Tests by this method on peroxide solutions of known concentration with and without hydrazine. proved its suitability.

The concentration of sodium hydroxide was varied from 0.0 to 0.46 *M*, the initial concentration of hydrazine from 0.07 to 0.27 M and the temperature from 20 to 25 and 30°. Air was used in place of oxygen only to determine the effect of oxygen pressure, as the rate of oxidation was much more rapid with pure oxygen. Runs were made in the presence of ammonia, hydronitric acid, hydrogen peroxide and sand, and with various rates of stirring and oxygen flow.

In the light of the results of Browne and Shetterly it was thought that hydronitric acid might be present but none could be found, though the tests are extremely sensitive. The solution also gave a negative test for nitrite and nitrate. Peroxide was shown to be present by the ether–dichromate test and also by the color reaction with titanium sulfate. The gases were tested for hydrogen with a palladium absorption tube but none could be found. In the early part of the work a small amount of ammonia was found in the more alkaline solutions. The amount was so small that it was not tested for in later runs.

An entirely different procedure was also used, shaking the solution in a bottle in

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[4] Bray and Cuy, THIS JOURNAL, 46,858 (1924).

the presence of oxygen, and the results are apparently of a different character. This report deals only with the bubbling method.

(2) Results.—In Fig. 1 is shown a series of characteristic curves for the auto-oxidation of hydrazine and the accompanying curves for the formation of peroxide. Data for some of the curves are given in Table I. For the sake of brevity the major part of the results is merely summarized (Table II).

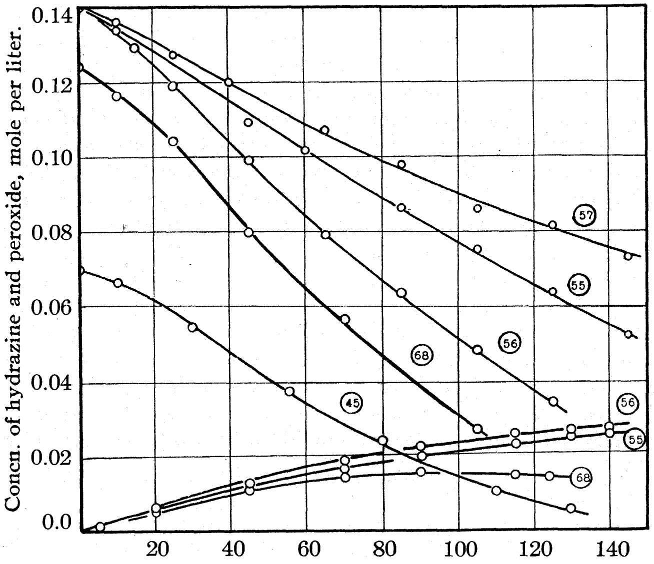

Fig. 1.—Oxidation of hydrazine and formation of peroxide. Upper curves, concn. of hydrazine; lower curves, concn. of peroxide. (57), NaOH = 0.00 *N*; (55), NaOH = 0.46 *N*; (56), NaOH = 0.15 N; (68), NaOH = 0.03 *N*; (45), NaOH = 0.03 *N*; Temp. = 20° in **Run** (45), 25° in others.

TABLE I

CALCULATION OF VELOCITY CONSTANT FOR THE AUTO-OXIDATION OF HYDRAZINE

$$k = \frac{1}{(t_2 - t_1)(1 - 1/n)} (C_1^{(1 - 1/n)} - C_2^{(1 - 1/n)})$$

Expt. 68 NaOH, 0.03; Temp., 25°			Expt. 57 NaOH, 0.00; Temp., 25°		
t	C	k	*t*	*C*	k
25 (t_1)	0.1038	...	25 (t_1)	0.1275	...
35	.0920	0.0036	45	.1162	0.0016
45	.0802	.0038	65	.1065	.0016
55	.0700	.0037	85	.0970	.0015
65	.0602	.0038	105	.0880	.0015
75	.0512	.0038	125	.0805	.0015
85	.0425	.0039	145	.0740	.0014
105	.0274	.0039			

TABLE I (*Concluded*)

t	C	k	t	C	k
Expt. 45 NaOH, 0.03; Temp., 20°			Expt. 62 NaOH, 0.03; Temp., 25°		
20 (t_1)	0.0620	...	15 (t_1)	0.2562	...
30	.0545	0.0032	35	.2170	0.0041
40	.0475	.0032	55	.1820	.0040
50	.0410	.0032	75	.1475	.0041
70	.0285	.0033	95	.1155	.0042
90	.0182	.0033	115	.0850	.0043
110	.0107	.0033			
130	.0062	.0033			

TABLE II

SUMMARY OF EXPERIMENTAL DATA ON AUTO-OXIDATION OF HYDRAZINE AT 25°

Expt.	Orig. concn. of hydrazine, mole/liter	Concn. of NaOH	Peroxide present when 0.05 mole of N_2H_4 is oxidized	k	Remarks
52	0.1392	0.03	0.013	0.0037	
54	.1398	.03	.013	.0038	
60	.0672	.03	.012	.0042	
62[a]	.2646	.03	.013	.0041	
68[a]	.1243	.03	.012	.0038	6 months after 52-54
69	.1243	.03	.012	.0033	0.015 M NH_3 present
70	.1232	.03	.011	.0038	0.015 M NH_3 present
71	.1232	.03	.012	.0038	0.0001 M HN_3 present
53	.1232	.012	.012	.0039	
74	.1436	.012	.010	.0035	6 months after 53
58	.1398	.15	.019	.0032	
56	.1398	.15	.018	.0034	
55	.1398	.46	.018	.0021	
59	.1398	.46	.018	.0022	
57"	.1398	.00	.022	.0015	
76	.1263	.03	.011	.0020	1 g. Ottawa sand added
45"	.0699	.03	.014	.0032	Temp., 20°
46	.1398	.03	.010	.0056	Temp., 30°
64	.1366	.03	.002	.0042	0.0167 M H_2O_2 present
44	.0699	.46	(.020)	.0013	Temp., 20°
63	.1398	.03	Extrap. (.009)	$-dc/dt$ = .0002	Air instead of O_2

[a] Full data in Table I.

(3) Discussion. (a) The Effect of Hydrazine Concentration.—The curves all show for the oxidation of hydrazine a characteristic double inflection, with a period of "induction" at the beginning followed by a rapid change of slope, after which they assume a slight concavity to the horizontal axis. After the first period of irregular change all, covering a fourfold increase in hydrazine concentration, may be formulated by the equation developed by Bodenstein[6] for certain gas reactions and adapted by MacInnes[6] to a heterogeneous reaction in solution whose rate is governed by the adsorption of the reactants, or diffusion

$$-\frac{dC}{dt} = k\cdot C^{\frac{1}{n}}$$

Since it is not possible to begin the calculations with zero time, it is necessary to calculate the constants from point to point or better to adopt some one point as a basis. In either case

$$k = \frac{1}{(t_2 - t_1)(1 - 1/n)}\left(C_1^{(1 - 1/n)} - C_2^{(1 - 1/n)}\right)$$

A value of 2 for "*n*" proved to satisfy the conditions satisfactorily over the whole range of temperature and concentration. It might be expected that a different value would be required at different temperatures, but a similar small variation of "*n*" with temperature has been noted in another similar heterogeneous reaction.[7] A certain drift should be expected in these constants because there is unavoidably some loss of hydrazine by volatilization. This is a variable quantity depending upon duration of experiment and alkalinity of solution but present in all cases. Rough experiments using hydrogen instead of oxygen indicated a maximum loss of 2% an hour. This being a heterogeneous reaction it was difficult to obtain results which agreed as closely as 2% and no correction was made for the loss. Duplicates run at periods of three to six months agreed in quite a satisfactory manner, as may be seen from the tables.

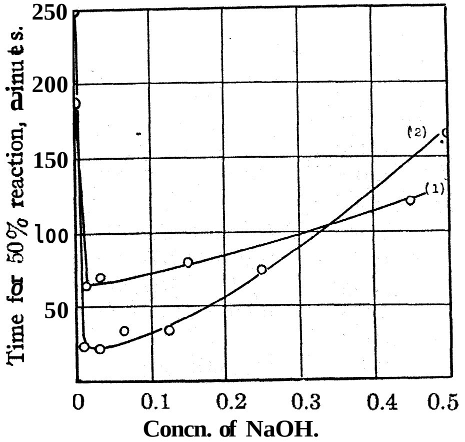

Fig. 2.—Comparison of effect of NaOH on auto-oxidation of hydrazine (1) and on the catalysis of hydrogen peroxide by colloidal platinum (2).

(b) The Effect of OH– Concentration.—The effect of increasing the hydroxyl-ion concentration is first to accelerate oxidation and then to retard it. The maximum rate of oxidation is found when the sodium hydroxide concentration is 0.01–0.03 M. An interesting coincidence occurs here. Inspection of Fig. 2 shows that the effect of sodium hydroxide on this reaction is practically the same as its effect on the catalysis of hydrogen peroxide by colloidal platinum.[8] It is difficult to ascribe this effect to some

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[5] Stock and Bodenstein, *Ber.*, 40,570 (1907).

[6] MacInnes, THIS JOURNAL, 36,878 (1914).

[7] Sieverts and Peters, *Z. physik. Chem.*, *91*, 199 (1916).

[8] Bredig and Müller von Berneck, *ibid.*, 31,258 (1899).

particular part of the phenomenon, because the maximum rate of oxidation is attended by a minimum formation of peroxide (see paragraph c). Whether the smaller amount of peroxide is present at this concentration (NaOH = 0.01–0.03 M) because this represents the optimum condition for the decomposition of peroxide (Fig. 2) is not certain. It is fairly certain, however, that the amount of peroxide present is the resultant of two reactions, one of formation and one of decomposition, since in some cases the amount passes through a maximum and decreases (see Run 68, Fig. 1).

A possible explanation of the effect of sodium hydroxide on the oxidation is this. The molecule N_2H_4 may be the oxidizable material. Low concentrations of NaOH serve to repress the ionization of hydrazine hydrate, thus increasing the concentration of the N_2H_4 molecules. It also combines with the peroxide formed. High concentration may alter conditions such as hydration, association, etc., so as to reduce the actual number of reactive molecules. It might be thought that the formation of peroxide would reduce the hydroxyl-ion concentration to an extent sufficient to affect the course of the reaction. A rough calculation shows this not to be the case.

$$\frac{N_2H_5^+ \times OH^-}{N_2H_4} = 1.5 \times 10^{-6}$$

In a solution where NaOH = 0.03 M, as a first approximation then

$$\frac{N_2H_5^+}{N_2H_4} = 5 \times 10^{-5}$$

The hydrazine is practically un-ionized. At the end of two hours the peroxide concentration was about 0.015 M. Assuming that the sodium salt is not hydrolyzed, the effective OH^- is still 0.015 and the ratio is

$$\frac{N_2H_5^+}{N_2H_4} = 1 \times 10^{-4}$$

Since the molecule is presumably the reactive form, this difference in ratio can have no detectable effect on the reaction from the standpoint of hydrazine concentration.

(c) The Effect of Peroxide Concentration.—It has not been found possible to formulate any satisfactory expression for the increase of peroxide with time, probably because it is the difference between formation and decomposition. Run 76 in which standard Ottawa sand was added shows a lower amount of peroxide than usual, substantiating this theory. The amount of peroxide varies with the initial concentration of hydroxyl ion almost in inverse ratio to the rate of oxidation, *i. e.*, slow oxidation, high peroxide and *vice versa* as may be seen by comparing companion curves in Fig. 1. It does not necessarily follow that the peroxide is low because it is reacting or has reacted with hydrazine, thereby accelerating the rate, because when air is used instead of oxygen, the rate of oxidation falls to one-fifth, but the amount of peroxide does not decrease accordingly. In Run 64, however, in which 0.0167 M peroxide was added at the start, the oxidation seems to run slightly faster, but the interesting thing is that the peroxide formed in the run is less than 30% the normal amount formed in a similar run with no added peroxide.

As judged by the amount of peroxide formed when 0.05 mole of hydrazine has been oxidized, see Col. 4, Table II, it seems probable that in the absence of NaOH the ratio Moles peroxide formed/Moles hydrazine oxidized = 1:2. In the presence of low OH– (0.012–0.03) the ratio is 1:4 and in strong NaOH (0.15–0.46) the ratio is 1:3. Since, however, different time intervals are required in the several cases for this amount of oxidation, no very close distinctions may be drawn. It should be stated that the formation of peroxide is not a function of this apparatus or procedure. It is formed by simple exposure of an alkaline solution of any hydrazine salt, or hydrazine hydrate, on a watch glass to air, though, of course, not so rapidly as with pure oxygen.

(d) The Temperature Effect.—In 0.03 N NaOH, k for the oxidation increases from 0.0032 at 20° to 0.0056 at 30°, giving a coefficient of 1.75 for this ten-degree interval. This corresponds more closely to that of a chemical reaction at a surface than to a diffusion process.[9]

(e) The Active Surface.—The data so far obtained indicate, therefore, a reaction at a surface, but it is not certain what this surface may be. The walls and stirrer were coated with paraffin, upon which very little reaction would be expected. The fritted glass disk falls under suspicion, but addition of sand which should increase such surface cuts the velocity in half. The bubbles of oxygen were extremely fine but they passed through the solution rather rapidly. The temperature coefficient and indeed the expression for the velocity constant correspond to a micro-, rather than macro-heterogeneous reaction, so it is possible that this is a reaction catalyzed by dust particles.[10] In preliminary experiments it was found that variously prepared samples of hydrazine sulfate gave very great differences in rate, most easily explained by this same hypothesis.

(f) The Effect of Oxygen Pressure.—When air was used the rate was so slow that the curve was practically a straight line after an initial drop. The slope of this line was 0.0002 as compared with a slope of 0.00107 for a similar solution using oxygen. This ratio is within the limit of experimental error 1:5. In other words, the reaction rate is directly proportional to the partial pressure of oxygen. A 30% increase in oxygen flow above that ordinarily used had no detectable effect on the rate of oxidation.

(g) The Effect of Added Impurities.—Ammonia (0.015 M) was added in two runs. No effect could be noted. Two runs with small amounts of hydronitric acid added likewise showed no difference from the ordinary. These two substances were added because they are the most common prod-

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[9] Denham, *Z. physik. Chem.*, **72, 687 (1910).**

[10] **Rice, THIS JOURNAL, 48, 2909 (1926).**

ucts of oxidation of hydrazine with the exception of nitrogen itself. Qualitatively it was found that the reaction, like other auto-oxidations, is affected by substances like acetanilide, aniline, hydroquinone, etc.

Summary

1. The auto-oxidation of hydrazine in alkaline solution has been studied by the procedure of passing oxygen through a fritted glass disk into the solution.

2. With this procedure the reaction is heterogeneous and the rate may be expressed by the equation $-dC/dt = k \times p_{O_2} \times C^{1/n}$, being governed by the rate of adsorption of hydrazine on the active surface.

3. Hydrogen peroxide is formed under all conditions when hydrazine in dilute alkaline solution is exposed to the action of oxygen.

4. The rate of oxidation passes through a maximum, in the presence of sodium hydroxide, with increasing concentration of hydroxide. The optimum concentration corresponds with that for the maximum rate of decomposition of hydrogen peroxide by colloidal materials, indicating that the auto-oxidation is also a micro-heterogeneous reaction.

CORVALLIS, OREGON

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

OZONIZATION AND INTERACTION OF OXYGEN WITH NITROGEN UNDER ALPHA RADIATION

BY S. C. LIND[1] AND D. C. BARDWELL[2]

RECEIVED MAY 22, 1929 PUBLISHED SEPTEMBER 5, 1929

The following experiments were made about three years ago as a part of our general study of chemical reactions produced by alpha rays. Detailed publication[3] was delayed in the hope that the work could be made more complete in certain respects. Recent results of others for the same reactions, but using high-speed cathode rays, which will be fully discussed later, indicate that maximum yields per ion pair can be approached only with such high rates of gas flow and with such low intensity of discharge that it appears uninviting to attempt with alpha radiation to push farther in either of these directions than has already been done. The results given here for the formation of oxides of nitrogen, although rather incomplete, represent the first ionic yields to be reported for this important reaction.

Ozonization.—The production of ozone is studied both in pure oxygen and in mixtures with nitrogen. This was begun as a continuation

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[3] Brief mention was made of the results in "Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., New York, 1928, 2d ed., pp. 83 and 92.

of the earlier work of Lind[4] whose results showed considerable fluctuation in yield, believed to have been due to accidental small amounts of mercury in the ozonizing chamber, which caused high and variable de-ozonization.

More recently D'Olieslager[5] has reported new results in ozonization by alpha rays. In a static system of oxygen mixed with radon he found little or no ozone, but upon adopting the original method of Lind[4] of flowing oxygen past an alpha ray bulb and measuring ozone chemically in the effluent gas, he was able to obtain a yield of ozone of 1 molecule per ion pair, or twice the maximum obtained by Lind. He furthermore made the important observation that the yield is a function of the flow and of the intensity of radiation so that owing to de-ozonization by the alpha rays the net yield per ion pair is highest for the lowest concentration of ozone.

Experimental

The present experiments were made also using the original method except for elaborate precautions against the presence of mercury in the ozonizing chamber or flow system. While the new results (Table II and Fig. 1) are not without some fluctuation, they show great improvement over the original ones. They confirm D'Olieslager's claim of dependence of yield on ozone concentration, and under the best conditions show yields considerably higher than his. This point will be discussed further.

D'Olieslager[5] first suggested a method of calibrating the alpha-ray bulb system for ionization by means of a reaction of known M/N ratio. The failure in employing acetylene polymerization ($M/N = 20$) and the later success with $2C0 + O_2 = 2CO_2$ ($M/N = 6$) have been discussed elsewhere by one of us.[6] The latter method was employed for standardization in the present work. Electrolytic gas ($2H_2 + O_2 = (2H_2O)$; $-M/N = 6$) may be employed even more conveniently, but preferably at double the

TABLE I

CALIBRATION OF ALPHA-RAY BULB SYSTEM FOR IONIZATION BY THE REACTION $2CO + O_2 = 2CO_2$ (ABSORBED IN CAUSTIC)

$E_0 = 0.1975$ curies; vol. of reaction bulb, 518.3 cc.; of absorbing bulb, 27.0 cc.; of trap, 3.4 cc.; of connecting tubes, 11.0 cc.; total vol., 563.7 cc.

Date	Hour	Time days	Time hrs.	$e^{-\lambda t}$	Vol. of gas, N. T. P., cc.	Vol. change per curie. (press. const.), cc.
Aug. 11	4:00 P.M.	0	0.0	1.00000	527.59	...
Aug. 11	9:30 P.M.	0	5.5	1.95959	522.28	665.4
Aug. 12	1:00 P.M.	0	21.0	1.85428	506.56	756.4
Aug. 12	11:00 P.M.	1	7.0	1.79255	496.83	795.0
Aug. 13	8:30 A.M.	1	16.5	1.73805	488.28	794.0

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[4] S. C. Lind, *Sitzb. Akad. Wiss. Wien, 120,* 1709 (1911); Am. *Chem.* J., 47, 397 (1912).

[5] J. D'Olieslager, Bull. *Acad. Roy. Belg., 12,* 719 (1925).

[6] Lind, ref. 3, p. 90.

pressure of the $2CO + O_2$ mixture on account of the lower stopping power of hydrogen for alpha rays. The pressure of either mixture should be so regulated that the ionization produced by an alpha particle in traversing the radius of the reaction sphere shall fall in the same range as that of the gas to be experimented with. As the first example of the employment of this method of calibration, a set of data is given in Table I.

Taking **794.5** as the best value for the volume change per curie, the number of molecules reacting per curie is

$$7.945 \times 10^2 \times 2.705 \times 10^{19} = 21.5 \times 10^{21}$$

Taking

$$\frac{-M_{(CO+O_2)}}{N_{(CO+O_2)}} = 6 \quad \text{or} \quad \frac{+M_{CO_2}}{N_{(CO+O_2)}} = 4$$

the number of ions produced in the gas per curie would be

$$\frac{21.5 \times 10^{21}}{6} = 3.58 \times 10^{21}$$

Using Bragg's value of **1.13** of k for O_2 and **1.015** for CO, the number of ions would be **1.13** X **3.4** X 10^{21} = **3.85** X 10^{21}.

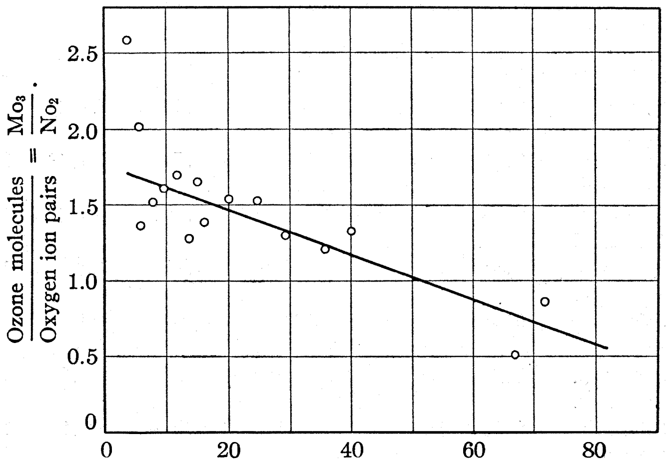

Fig. **1.**

Examination of Table II and Fig. 1 will show that the M/N ratio varies from **0.5** to about **1.7** as the ozone concentration decreases from about **70** parts per million to **10** parts per million. There is one value of 2.6 for M/N and another of **2.0,** but these two values are probably not consistent with the others. Values of M/N have been plotted against concentration of ozone. The values are quite irregular but there is a definite trend toward higher values of M/N as the concentration of ozone approaches zero.

Discussion of Results on **Ozonization.**—At present it is not possible to

TABLE II

SUMMARY OF RESULTS ON OZONE FORMATION BY IONIZATION OF OXYGEN

Date	Hour	Milli-curies decayed	O_2 flow, cc/min.	O_2 flow over total interval, cc.	Ozone formed, cc.	Concn. of ozone in parts per million		$\frac{M_{O_3}}{N_{O_2}}$	
6/25	4:00 P.M.								
6/25	10:15 P.M.	4.03	20	5.1×10^3	0.396	79	72	0.69	0.86
6/25	10:15 P.M.								
6/26	8:30 A.M.	6.23	20	12.3×10^{13}	.860	70		.97	
6/26	9:45 A.M.								
6/26	9:30 P.M.	6.5	10	7.05×10^{13}	.472	67		.51	
6/26	9:45 P.M.								
6/27	2:00 P.M.	8.16	40	39.0×10^{13}	1.553	40		1.33	
6/27	2:00 P.M.								
6/28	8:30 A.M.	8.16	35	39.0×10^{13}	1.39	35.6		1.21	
6/28	8:30 A.M.								
6/29	8:30 A.M.	9.11	100	144×10^{13}	2.16	15		1.66	
7/2	1:00 P.M.								
7/3	8:30 A.M.	3.48	160	178×10^{13}	1.00	5.6		2.02	
7/3	8:45 A.M.								
7/4	11:00 A.M.	3.94	52	81.9×10^{13}	0.953	11.6		1.70	
7/4	11:00 A.M.								
7/5	4:30 P.M.	3.60	25	44.3×10^3	.713	16.1		1.39	
7/5	4:30 P.M.								
7/6	3:00 P.M.	2.28	15	20.2×10^3	.498	24.6		1.53	
7/6	3:00 P.M.								
7/7	3:00 P.M.	2.02	150	216×10^3	.746	3.46		2.59	
7/7	3:00 P.M.								
7/9	8:30 A.M.	2.78	15	37.4×10^3	.507	13.6		1.28	
7/17	11:00 A.M.								
7/18	8:00 A.M.	20.8	100	132×10^3	3.87	29.3		1.30	
7/18	9:00 P.M.								
7/19	8:30 A.M.	9.1	150	1000×10^3	1.99	20		1.54	
7/22	8:30 A.M.								
7/23	8:30 A.M.	9.55	150	216×10^3	2.13	9.9		1.57	
7/23	8:30 A.M.								
7/23	3:30 P.M.	2.53	150	63×10^3	0.578	9.2		1.61	
7/23	3:30 P.M.								
7/24	8:30 A.M.	5.62	150	153×10^3	1.21	7.9		1.52	
7/24	8:30 A.M.								
7/25	11:30 A.M.	7.32	150	243×10^3	1.425	5.9		1.37	

predict *a priori* the yield per ion pair for a given reaction. Empirical rules have been established[7] by analogy for certain classes of reactions, but since ozonization represents a unique class, namely, a system of a single component with supposed affinity for free electrons, we have no guiding precedent. Evidently, unlike the case of components with no electron affinity, we must consider negative as well as positive ions. The negative ions

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[7] Ref. 3, Chapter 5.

would be molecular and if we assume that the positive ions are also mainly molecular,[8] the following might represent some of the possibilities.

TABLE III

THEORETICAL O_3 YIELD

	Reactions		Per ion pair	Remarks
	No ion clustering			
1	$O_2^+ + O_2^- = O_3 + O$	rare	$>1 <2$	The O atom in (1) must have high velocity to carry away the heat of the ion recombination, to prevent decomposition of O_3
1a	$O +$ 0 2 $= O_3$			
1b	$O + O_3 =$ 202			
1c	$O + O = O_2$			
	Bimolecular clusters			
2	$O_2^+ \cdot O_2 + O_2^- \cdot O_2 = 2O_3 + O_2$		2	Improbable that $2O_3$ and O_2 would all remain intact
2a	$O_2^+ \cdot O_2 + O_2^- \cdot O_2 = 2O_3 +$ 2 0		$>2<4$	
	Stoichiometric clusters			
3	$O_2 \cdot O_2^+ \cdot O_2 + O_2 \cdot O_2^- \cdot O_2 = 4O_3$		<4	Improbable that all 4-03 molecules would remain intact

If any such reactions take place as those indicated above, yields could be expected in the range 1 to 4 molecules of O_3 per ion pair in oxygen. Although Mund and D'Olieslager[9] deduced from experiments in the presence of mercury that the maximum theoretical yield does not exceed about 1, the present results show it cannot be less than 1.5, is more probably nearer 2, while results of less certainty indicate it to be as high as 2.0 to 2.6. Undoubtedly secondary de-ozonization plays the controlling part, but it does not appear possible that it is caused by direct collision of alpha particles with O_3 molecules as has been suggested. We know the action of alpha particles is not in the least selective and therefore the chance of de-ozonization by this means at low concentration of O_3 is practically negligible. Evidently we must resort to a de-ozonizing action of activated oxygen either as ions or as atoms (see Reaction lb).

Owing to the great difficulty of working at yet lower ozone concentration or of extrapolating, since the experimental results become progressively less accurate in that direction, it is not possible to set an upper limit to the yield, but there is no indication from alpha ray results that it would exceed 3–4 molecules of ozone per ion pair in oxygen.

Using high velocity cathode rays from a Coolidge tube, Busse and Daniels[10] have recently obtained results which confirm the ionic yields obtained with alpha rays. Since they could not measure nor calculate ionization directly, they employed the indirect method of measuring calorimetrically the energy received in their reaction chamber. Assuming it to be wholly expended in producing O_2^+ ions by electron collision, with a loss of 15 volts (the ionization potential of O_2) they obtained a yield of $M_{O_3}/N = 1$.

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[8] H. D. Smyth, *Proc. Roy. Soc. London*, 105A, 116 (1924).

[9] W. Mund and J. D'Olieslager, Bull. *Acad. Roy. Belg.*, Nos. 4–5 (July).

[10] Busse and Daniels, THIS JOURNAL, 51, 3271–3286 (1929).

The earlier work of Krüger[11] with cathode rays accorded with the alpha ray results and hence with the new results of Busse and Daniels, but in later work Krüger and Utesch,[12] measuring the ionization by a supposed saturation current method, obtained much higher yields, 12 to 40 molecules of O_3 per ion pair in O_2. If, however, Krüger and Utesch were misled in believing they secured saturation current, as seems very probable on *a priori* grounds,[13] their ionization measured was too low, and hence their calculated yield too high. That this was probably the case is indicated by the fact that both Busse and Daniels and Marshall[14] have attempted to obtain saturation current under conditions similar to those of Krüger and Utesch without any indication that saturation was approached. There remains then every reason to believe that the law of equivalence of ionization and chemical action, first established for alpha rays, holds in the same way for Lenard rays. Busse and Daniels' calorimetric method of arriving at an M/N ratio is an important step in making such comparisons possible.

Interaction of Nitrogen and Oxygen. (Preliminary Experiments.)—It is rather striking that in all the gaseous reactions under alpha radiation that have been investigated, no results have been reported of the combination of oxygen and nitrogen under its influence, except a note by Soddy[15] who found that the collection of pure radon by condensation at low temperature is impossible if air is present in the gases, owing to the production of N_2O, which is also condensed at liquid-air temperature. The first compound formed in the arc process and in the oxidation of NH_3 is NO. The NO is oxidized to NO_2 (in equilibrium with N_2O_4) rather slowly in the presence of excess O_2. If NO_2 is dissolved in H_2O, HNO_2 and HNO_3 are formed in solution and some NO is liberated. This NO will oxidize to NO_2 in the presence of O_2, so that eventually all of the nitrogen is oxidized to nitrate.

Study of the combination of nitrogen and oxygen by alpha rays is greatly complicated by the simultaneous formation of ozone. A flow system was adopted like that recently used for ammonia synthesis.[16] Owing to the difficulty of determining the oxides of nitrogen and ozone separately in a flow system, the device was adopted of making alternate measurements of the total acidity by passing the gases for a time through standard alkali and then of the combined power to liberate iodine from a potassium iodide

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[11] F. Krüger, *Physik. Z.*, **13, 1040 (1912)**; "Nernst Festschrift," pp. **240–251 (1912)**.

[12] F. Krüger and O. Utesch, *Ann. Physik*, (4) *78*, **113–156 (1925)**.

[13] Lind, *Trans. Am. Electrochem. Soc.*, **53**, 26 **(1928)**.

[14] A. L. Marshall, THIS JOURNAL, **50, 3178 (1928)**.

[15] F. Soddy, "**Annual** Report of the Chemical Society" for **1910.** Vol. **8,** 299–300 **(1911)**.

[16] Lind and Bardwell, THIS JOURNAL, **50, 745 (1928)**.

solution. The oxides of nitrogen dissolving in alkali form nitrites and nitrates. The neutralizing capacity of the gas is thus a measure of the acid oxides formed and does not exceed one molecule of acid for each atom of nitrogen in the oxides. The capacity to liberate iodine is a measure of the combined oxidizing power of ozone and nitrogen oxides. All oxides of nitrogen are oxidized to N_2O_5 by ozone providing the latter is in sufficient excess. That the concentration of ozone was not always high enough to oxidize completely the nitrogen oxides to N_2O_5 in the time allowed before absorption seemed to be indicated by the results for air in which there was a marked "after-bluing" in the thiosulfate titration—in some cases amounting to 25% of the total titration. In mixtures of air and oxygen the extent of "after-bluing" became less for increasing O_2 content.

The ratio of oxygen to nitrogen was varied from that in air to about 4 O_2:-1N_2 by the addition of oxygen to the stream. The total oxidizing power is found to be equivalent to 2.4 molecules of ozone per pair of ions (total) in air and decreases slightly as the mixture becomes richer in oxygen. The results are shown in Table IV.

TABLE IV

RESULTS WITH ADDED OXYGEN

Date	Hour	Flow, cc. per min.		Ratio		Milli-curies decayed	$\frac{M_{\text{acidity}}}{N_{\text{total}}}$	$\frac{M_{\text{ozone equiv.}}}{N_{\text{total}}}$
		O_2	Air	O_2	N_2			
6/22–6/23	3:30 P.M.–8:45 A.M.	..	20	1	4	18.45	0.74	..
6/23–6/23	9:15 A.M.–2:15 P.M.	..	20	1	4	4.9	..	2.4
6/23–6/24	3:30 P.M.–8:30 A.M.	..	20	1	4	15.2	0.77	...
6/24–6/25	2:45 P.M.–8:30 A.M.	9.0	16.0	1	1	13.3	0.49	...
6/25–6/25	8:45 A.M.–1:45 P.M.	9.0	16.0	1	1	3.43	..	2.2
6/29–6/30	1:15 P.M.–9:30 P.M.	60	20	4	1	6.18	..	2.2
6/30–6/30	11:00 A.M.–9:30 P.M.	60	20	4	1	2.83	..	2.3
6/30–7/1	9:30 P.M.–9:00 A.M.	30	10	4	1	2.85	..	1.8
7/1–7/2	10:15 A.M.–8:30 A.M.	30	10	4	1	4 81	0.23	..
7/15	5:00 P.M.	Closed the reaction bulb off containing tank O_2						
7/16	12:00	Started sweeping out with O_2 at 50 cc. per min.						
7/16	2:00 P.M.					28.5	0.005	
7/19	11:00 A.M.	Closed the reaction bulb off containing air						
7/20	4:00 P.M.					19.5	0.23 cc. of N_2O	
							$\frac{M_{(N_2O)}}{N_{(\text{total})}} = 0.076$	

It is quite apparent that the formation of acidic oxides falls off as the N:O ratio in the flowing gases is diminished. Apparently this might mean that nitrogen ions, but not oxygen ions, are responsible for this reaction. If the ionization potential of nitrogen is higher than that of oxygen, then ionization by collision of the second kind[17] could take place only in the direction $N_2^+ + O_2 = N_2 + O_2^+$ which would explain at once why nitrogen oxide formation diminishes while total oxidation remains relatively little changed,

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[17] G. P. Harnwell, Phys. *Rev.*, 29, 683, 830 (1927).

since the latter represents both ozone and oxides of nitrogen. In the static experiment with 28.5 millicuries of radon decaying in a 4 O_2:1 N_2 mixture, very little acid was produced.

The special experiment on the production of nitrous oxide in air confirmed Soddy[15] in its formation, although the yield was only 0.076 molecules per pair of ions, much lower than that of the acid-forming oxides.

The nitrous oxide was separated from the air by use of liquid air and was subsequently pumped off at $-100°$ into a miniature eudiometer tube. That the gas so separated was nitrous oxide was confirmed by explosion with a measured volume of pure hydrogen. The volume contraction corresponded approximately to that for the reaction $N_2O + H_2 = N_2 + H_2O$ (liq.).

Summary

1. Ozonization in oxygen flowing past an alpha-ray bulb is higher (per ion pair) the faster the rate of flow and the lower the intensity of ionization, that is, higher the lower the ozone concentration from either influence, owing to de-ozonization. This confirms D'Olieslager's results.
2. The maximum yields of ozone obtained per ion pair (M_{O_3}/N_{O_2}) was not less than 1.5 and may be as high as 2–2.5.
3. De-ozonization appears to be due to a secondary effect of oxygen ions (or atoms), not to a primary impact with an alpha particle.
4. In mixtures of nitrogen and oxygen both ozone and acid-forming oxides of nitrogen are simultaneously formed; also a smaller amount of nitrous oxide (confirming Soddy). Nitrous oxide formation was investigated only for air.
5. The yield of acid-forming oxides diminishes with decreasing N_2:O_2 ratio, while the total oxidizing power toward potassium iodide solution is little influenced. A theory is proposed for this.

MINNEAPOLIS, MINNESOTA

NOTES

An Application of the Thiocyanate Method for the Precipitation of Copper in the Confirmatory Tests for Cadmium and Antimony.—The use of the thiocyanate anion as a means for the separation of copper from cadmium, after first having reduced the copper with sulfurous acid, has been suggested by Crookes.[1] This method has also been used for the quantitative determination of copper, but to the knowledge of the author it has not hitherto been applied to the qualitative scheme of analysis. The insolubility of cuprous thiocyanate in dilute sulfuric and hydro-

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William Crookes, "Select Methods in Chemical Analysis," Longmans, Green and Company, London, 1886, p. 332.

chloric acids and the ease of precipitation makes it well suited for this application.

The means for the separation of copper from cadmium in the confirmatory test for cadmium given by Noyes[2] has been found to be not quite satisfactory for class use due to the fact that many times the student does not obtain a thorough separation of the copper.

The thiocyanate method has been used in the classes in the Qualitative Laboratory of the University of New Hampshire and has been found to give very satisfactory results.

The procedure for this method is as follows. To the part of the ammonium hydroxide solution remaining after the ferrocyanide test has been made for the confirmation of copper add dilute sulfuric acid until acid to litmus, then 5 cc. of a normal solution of potassium thiocyanate. A brown coloration will result due to the formation of cupric thiocyanate. Heat to boiling, add about 0.5 g. of dry sodium sulfite and continue boiling for about one minute until the white precipitate of cuprous thiocyanate has coagulated. Filter off the precipitate and saturate the clear filtrate with hydrogen sulfide. If cadmium is present the characteristic yellow precipitate of cadmium sulfide will form.

This reagent has also been used to advantage to avoid the interference of copper in the test for antimony as given by Noyes,[3] which occurs in some instances when sodium polysulfide is used and very often when ammonium polysulfide is employed for the separation of the copper and tin groups. The above procedure may be used after the antimony and tin have been separated from the arsenic by concentrated hydrochloric acid, and the solution has been diluted to the proper acid concentration for the precipitation of the antimony sulfide.

CONTRIBUTION FROM THE
CHEMICAL LABORATORIES OF THE
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ALBERT F. DAGGETT

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An Improved Stopcock for Gas Analysis Burets.—The usual type of buret stopcock used in both technical and exact gas analysis apparatus is of the three-way downward outlet type or a specially bored adaptation[1] of this when a compensator is attached. The objection to this type of stopcock lies not only in the difficulty of stopping the absorbent solutions exactly at the stopcock with its upward pointing outlet, but also in the

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[2] A. A. Noyes, "Qualitative Chemical Analysis," The Macmillan Company, New York, 1928, p. 80.

[3] Ref. 2, p. 86.

[1] A. H. White, "Gas and Fuel Analysis," McGraw-Hill Book Company, New York, 1st ed., 1913, pp. 16, 73.

unpreventable draining of these solutions into the gas buret during the absorption process. Even in the hands of an expert an exact gas analysis apparatus becomes badly fouled in the course of a single complete analysis of a gas mixture such as water gas.

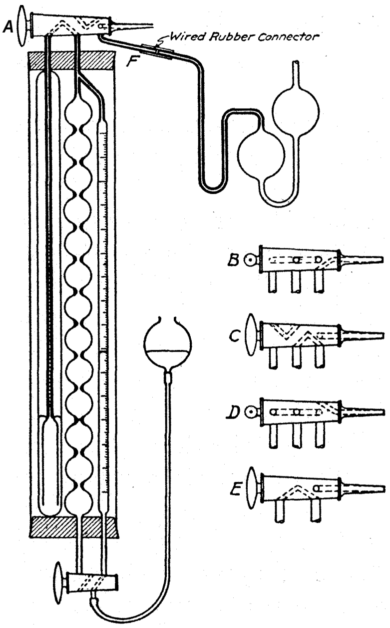

Fig. 1.

This difficulty is eliminated by the use of the special stopcock shown attached to a bulbed exact gas analysis apparatus[1] equipped with a single leg compensator[2] in Fig. 1. By placing the outlet to which the absorption pipet is attached below instead of above the stopcock barrel, it is possible to bring the absorbent solution slowly up to the bore of the cock without any danger of spilling over into the buret. During the absorption of any constituent the solution adhering to the walls of the stopcock outlet then drains down away from the stopcock and buret. Four views of the stopcock are shown at A, B, C and D, each a quarter turn in the clockwise direction from the preceding position as shown in the sketches. In the case of an uncompensated buret such as is used in technical analyses the simpler stopcock shown at E suffices.

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[2] F. C. Vilbrandt, *Ind. Eng. Chem.*, 16, 936 (1924)

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

ACYL DERIVATIVES OF ORTHO-AMINOPHENOL. V

BY R. E. NELSON AND H. S. ROTHROCK

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When diacyl derivatives of o-aminophenol are prepared by the usual methods, it is found in most cases that the order of introduction of the two different acyl groups has no influence upon the formation of the diacyl, identical products being isolated from the two acylations. The position of the acyl groups in the molecule can be determined by removing the group attached to oxygen by saponification with dilute alkali, and determiningfrom the physical constants of the remaining mono-acylated product the group attached to the nitrogen. The identical diacyls mentioned above are found to saponify to yield identical products, as would be expected.

The formation of identical rather than isomeric products on reversing the order of acylation indicates that during acylation a rearrangement must have occurred in one of the two cases. It is found that certain acyl groups have more power than others to bring about this migration, weight and acidity of the group being considered to have the predominating influence in their obtaining a position in the more basic amino group in preference to the phenol group.

Previous work on this subject by Ransom,[1] Ransom and Nelson,[2] Nelson and others,[3] and Raiford and others[4] is discussed in the literature.

The work of Ransom and of Ransom and Nelson indicated that, in the cases observed, carbalkoxy (COOR) groups had the power to displace carbonyl (COR) groups from their position on the nitrogen atom during the introduction of the second acyl group. Nelson, Shock and Sowers[5] found, however, that the n-carbopropoxy group, *n*-C_3H_7OCO, was displaced from the nitrogen atom by the benzoyl group, while the *iso*carbopropoxy group, *iso*-C_3H_7OCO, was able to displace the benzoyl group from the nitrogen. This peculiar action was also investigated by the present authors and the results were confirmed. It was found in addition, however, that rearrangement was not complete and that both possible monoacyls were produced on saponification. The identical diacyls may then have been either identical equilibrium mixtures or the same pure compound, in which last case rearrangement must have occurred during saponification.

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[1] Ransom, Am. *Chem. J.*, 23, 1 (1900).

[2] Ransom and Nelson, THIS JOURNAL, 36,390 (1914).

[3] Nelson and others, *ibid.*, 48, 1677 (1926); (b) 48, 1680 (1926); (c) 49, 3129 (1927); (d) 50,919 (1928).

[4] Raiford and others, *ibid.*, 41, 2068 (1919); (b) 44, 1792 (1922); (c) 45, 469 (1923); (d) 45,1728 (1923); (e) 46,430 (1924); (f) 46,2051 (1924); (g) 46,2246 (1924); (h) 46,2305 (1924); (i) 47, 1111 (1925); (j) 47, 1454 (1925); (k) 48,483 (1926).

[5] Nelson, Shock and Sowers, THIS JOURNAL, 49, 3129 (1927).

This investigation was undertaken with the view of determining whether any other differences in the action of *iso*- and n-acyl groups could be found, and to study a number of other carbalkoxy-benzoyl diacyl derivatives of o-aminophenol.

When o-benzoylaminophenol was acylated with *n*-butylchlorocarbonate, the same diacyl was obtained as when n-butyl-o-hydroxycarbanilate was acylated with benzoyl chloride. Saponification yielded in both cases n-butyl-o-hydroxycarbanilate, proving that in the diacyl the *n*-carbobutoxy group must have been attached to the nitrogen. In the first acylation, therefore, the benzoyl group rearranged to the oxygen.

In the same way, when o-benzoylaminophenol was acylated with *iso*-butylchlorocarbonate, the same diacyl was produced as when *iso*butyl-*o*-hydroxycarbanilate was acylated with benzoyl chloride. Here again saponification showed that the diacyl had the benzoyl group attached to the oxygen. In this case there is no difference in the action of the two pairs of isomeric carbalkoxy groups used against the benzoyl group.

Other structurally isomeric aliphatic acyl groups were next studied with the same purpose in mind. When o-benzoylaminophenol was acylated with n-valeryl anhydride, a diacyl, o-benzoylaminophenol n-valerate, was formed, while on treating o-n-valerylaminophenol with benzoyl chloride, an isomeric diacyl o-n-valerylaminophenyl benzoate, resulted. Saponification of each of these produced only o-benzoylaminophenol, indicating that in the latter case migration of the benzoyl group from the oxygen to the nitrogen must have occurred.

Similar results were obtained with the groups isovaleryl and benzoyl. Acylation of o-benzoylaminophenol with isovaleryl chloride produced a diacyl, o-benzoylaminophenyl isovalerate. Acylation of *o*-*iso*valerylaminophenol with benzoyl chloride produced a diacyl, *o*-*iso*valerylaminophenyl benzoate. Saponification of the first product yielded only *o*-benzoylaminophenol, while saponification of the latter yielded largely *o*-benzoylaminophenol and a small amount of o-isovalerylaminophenol. In this last case rearrangement is not quite complete during saponification. Obviously, however, the reaction is quite similar to that occurring in the case of the n-valeryl group.

When methyl o-hydroxycarbanilate was acylated with benzoyl chloride the same diacyl was produced as when o-benzoylaminophenol was acylated with methyl chlorocarbonate. Saponification of the diacyl yielded mainly o-benzoylaminophenol with a small amount of methyl *o*-hydroxycarbanilate.

The investigations up to this time on the benzoyl-carbalkoxy diacyl derivatives of o-aminophenol may be summarized in the following table.

The action of the carbomethoxy group may be explained as due to the difference in weight between it and the benzoyl group, but this does not

TABLE I

BENZOYL-CARBALKOXY DIACYL DERIVATIVES OF *o*-AMINOPHENOL

Croup used against benzoyl	Diacyl derivatives	Saponification product	Observer
CH_3OCO	Identical	CH_3OCO on O	Authors
C_2H_5OCO	Identical	C_2H_5OCO on N	Ransom
n-C_3H_7OCO	Identical	Mixture	Authors, Nelson and others
iso-C_3H_7OCO	Identical	*iso*-C_3H_7OCO on N	Nelson and others
n-C_4H_9OCO	Identical	*n*-C_4H_9OCO on N	Authors
iso-C_4H_9OCO	Identical	*iso*-C_4H_9OCO on N	Authors
iso-$C_5H_{11}OCO$	Identical	*iso*-$C_5H_{11}OCO$ on N	Ransom and Nelson

Ransom, Am. Chem. J., 23, 1 (1900); Nelson, Shock and Sowers, THIS JOURNAL, 49, 3129 (1927); Ransom and Nelson, *ibid.*, 36, 390 (1914).

explain why the only slightly heavier carbethoxy group acts differently, nor would it explain the behavior of the n-carbopropoxy group. Certain unknown factors must influence these rearrangements.

Experimental

All monoacyls were prepared by the method of Groenvik,[6] using *o*-aminophenol and the acid chloride. Their properties are summarized in Table II.

TABLE II

MONOACYL DERIVATIVES

Name	Formula	M. p., °C.	Yield, %	Analysis, N, % Calcd.	Found
o-n-Valerylaminophenol	$HOC_6H_4NHCOC_4H_9$	79	90	7.25	7.11
o-Isovalerylaminophenol	$HOC_6H_4NHCOC_4H_9$	100.5–102		7.25	7.13
Methyl *o*-hydroxycarbanilate	$HOC_6H_4NHCO_2CH_3$	122–123	75	8.38	8.20

The other monoacyls studied, which have been described previously, were prepared by the same method.

The diacyl derivatives of o-aminophenol were prepared by the Schotten-Baumann reaction and their properties are summarized in Table III.

TABLE III

PROPERTIES OF DIACYL DERIVATIVES

	Name	Saponification product
1	o-n-Carbobutoxyaminophenyl benzoate[a]	n-Butyl-o-hydroxycarbanilate
2	o-Isocarbobutoxyaminophenyl benzoate[a]	Isobutyl-o-hydroxycarbanilate
3	o-Benzoylaminophenylmethyl carbonate[a]	o-Benzoylaminophenol and some methyl o-hydroxycarbanilate
4	o-n-Valerylaminophenyl benzoate	*o*-Benzoylaminophenol
5	o-Benzoylaminophenyl n-valerate	o-Benzoylaminophenol
6	o-Isovalerylaminophenyl benzoate	o-Benzoylaminophenol and some o-Isovalerylaminophenol
7	*o*-Benzoylaminophenyl isovalerate[b]	*o*-Benzoylaminophenol

[a] The same product was formed when the acyl groups were introduced in the reverse order. [b] Prepared by the method of Einhorn and Hollandt, Ann., 301, 101 (1898).

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[6] Groenvik, Bull. *soc. chim.*, [2] 25, 173 (1876).

TABLE III *(Concluded)*

	Formula	M. p., °C.	Yield, %	Nitrogen, analyses, % Calcd.	Found
1	$C_4H_9CO_2HNC_6H_4OCOC_6H_5$	62.5	63	4.47	4.54
2	$C_4H_9CO_2HNC_6H_4OCOC_6H_5$	85.5–85.8	60	4.47	4.35
3	$C_6H_5COHNC_6H_4OCO_2CH_3$	128	78	5.17	5.07
4	$C_4H_9COHNC_6H_4OCOC_6H_5$	73–74	45	4.71	4.75
5	$C_6H_5COHNC_6H_4OCOC_4H_9$	103.5–104.5	36	4.71	4.73
6	$C_4H_9COHNC_6H_4OCOC_6H_5$	96–97.5	29	4.71	4.69
7	$C_6H_5COHNC_6H_4OCOC_4H_9$	113.5–117	35	4.71	4.57

Summary

1. A study has been made of the diacyl derivatives of o-aminophenol, using the benzoyl group against a series of carbalkoxy groups. It is found that the carbalkoxy group is able in most cases to displace the benzoyl group from the nitrogen. Where, however, there is a large difference in the weights of the two groups, as in the case of carbomethoxy (CH_3OCO) and the benzoyl (C_6H_5CO) groups, the benzoyl group is able to displace the lighter group completely, though the reverse takes place when the next heavier (C_2H_5OCO) group is used.

2. No evidence of differences in the action of *normal* and iso-acyl groups when used against the benzoyl group is observed in the case of the *n*- and *iso*carbobutoxy (C_4H_9OCO) groups and of the n- and *iso*valeryl (C_4H_9CO) groups.

3. New mono- and diacyl derivatives of o-aminophenol have been prepared and studied.

LAFAYETTE, INDIANA

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

THE EFFECT OF VARIOUS PREPARATIONS ON THE GROWTH OF BAKERS' AND BREWERS' YEASTS

BY ROGER J. WILLIAMS, MARION E. WARNER AND RICHARD R. ROEHM

RECEIVED NOVEMBER 26, 1928 PUBLISHED SEPTEMBER 5, 1929

In a previous paper[1] the fact was emphasized that different strains of yeast, all of which are called by the name *Saccharomyces cerevisiae,* may react quite differently toward nutrilites.[2]

Since this article was written considerable progress has been made in this Laboratory in concentrating the active material from yeast and other sources, the purification of which was the main object of our research. Before carrying the purification further we were interested to know how important the substance in question might be; whether, for example, it functions for one strain of yeast only or whether it might not be important in the nutrition of several strains of yeast. A second reason for making

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[1] Williams, Wilson and Von der Ahe, THIS JOURNAL, 49, 227 (1927).

[2] *See* Williams, *Science,* 67, 607 (1928).

this study, in addition to our interest in the significance of our own preparation, was that few controlled experiments have been reported in which different strains of yeast have been compared directly with each other and we deemed it important to know just how wide a variation might be expected.

The principal purpose of this paper, therefore, is to give results of experiments in which six strains of yeast (three bakers' and three brewers' yeasts) were compared with each other in their behavior toward various preparations, including the "α-Bios" and "β-Bios" of Eddy and Kerr,[3] "Bios I" (Inositol) of Lash Miller and our own concentrated material, as well as cruder preparations.

In Figs. 1–6 are given results in which crude yeast extract, prepared essentially according to the method outlined in the paper previously cited, was introduced in various amounts into our synthetic media and the growth of the different yeasts tested in the resulting solutions. The technique used was essentially that described previously, with a few minor modifications. Ten cubic centimeters of medium was used instead of 50. To it is added 1 cc. of a solution containing the material to be tested, plus 1 cc. of a yeast suspension (in sterile medium) of such concentration that the average for each large square on a Levy counting chamber was $3^1/_2$ to 4 cells. In these and other experiments in which a yeast crop was too small to weigh, the crop was estimated by visual comparison with suspensions containing known amounts of yeast. Neither this method nor that of weighing very small crops is highly accurate but they are sufficiently so for the purpose involved. In no case do we draw conclusions from small differences. In the experiments already mentioned, two sets of experiments were run in each case; one set was allowed to grow for eighteen hours and the other set for forty-eight hours.

The pure cultures of yeasts used in these tests were obtained from the following sources: Numbers **578** and **2335** from the American Type Culture Collection, Old Process Bakers' Yeast and Gebriide Mayer from the Fleischmann Company, Ruppert Brewing Yeast and Untergarige Hefe K from Dr. W. H. Eddy. "Old Process Bakers' Yeast," "Gebriide Mayer" and No. **2335** are bakers' yeasts and the others are, according to our best information, brewers' yeasts. We have been a little in doubt with regard to yeast No. 578, which has been used in this Laboratory most extensively in recent years. This culture originated in the collection of F. W. Tanner of the University of Illinois, which was handled by the American Type Culture Collection. It was first obtained with the understanding that it was bakers' yeast. In the late catalog of the American Type Culture Collection, however, it is listed as a brewers' yeast.

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[3] See Peskett, *Proc. Soc. Exptl. Biol. Med.*, **25**, **340** (1928).

Although the various yeasts grow at different rates and show other peculiarities, the following general observations may be made.

1. The growth of all the yeasts tested is remarkably stimulated by the addition of yeast extract to our synthetic medium. In all cases the maximum yeast crops were obtained when the largest amounts of extract were added.

2. When the yeast was allowed to grow for as long as forty-eight hours, there was a striking contrast between the control cultures and those in which very small amounts of extract were added.

3. When the yeast was allowed to grow for only eighteen hours, this contrast was less marked, yet the eighteen-hour growth curves are, in general, much more regular, approximating a straight line in the lower concentrations.

We believe that these results materially strengthen the suggestion previously made that a short growth period is superior to longer growth periods for quantitative measurements of dosage. Accordingly the rest of the experiments reported in this paper were carried out using the eighteen-hour growth period.

In Table I are given results of experiments in which the six yeasts are tested on two of our preparations, each added separately and both added together. Results reported previously showed that for yeast No. 578 two complementary preparations could be obtained. One fraction is adsorbed by fuller's earth; the other is not. Both together are necessary to stimulate appreciably the growth of this yeast. The preparations used in this experiment were (1) the crude unadsorbed residue obtained by treating the yeast extract with fuller's earth and evaporating the filtrate to dryness, *(2)* a highly concentrated material (Z_2) derived from the fraction which is adsorbed by fuller's earth from yeast extract.

The method of preparation of "Z_2" will not be described in great detail since we do not claim that the material is pure in any sense, and because we have subsequently materially modified our procedure for concentrating such material. Its preparation involved the following steps: (1) The "activated" fuller's earth was extracted with baryta, the baryta removed by sulfuric acid and the filtrate evaporated to dryness. *(2)* The residue was fractionated with the following solvents: 80% alcohol, water and methanol. In this process the activity was concentrated to approximately one-fifth of its original weight by applying the solvents in the order indicated and rejecting the insoluble material in each case. The Z_2 preparation is highly soluble in water. **(3)** The remaining soluble material was fractionated, following the method of Jansen and Donath,[4] the Z_2 coming from the fraction precipitated between the P_H values 6.5

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[4] B. C. P. Jansen and W. F. Donath, *Nededeel. Dienst Volksgezondheid Nederland, Indië*, **Part** I, 86–99 (1927).

and 7.5. Other fractions, however, also contained much activity. (4) The silver precipitate was decomposed with hydrochloric acid and carefully evaporated to dryness. The gummy residue constitutes "Z_2."

TABLE I[a]

EFFECT OF UNADSORBED RESIDUE AND Z_2 CONCENTRATE ON SIX YEASTS

Yeast	Blank	8 Mg. of U. R.	0.005 Mg. of Z_2	8 Mg. of U. R. +0.005 Mg. of Z_2
578	0.2	0.5	0.3	6.5
G. M.	.6	9.7	1.6	12.1
O. P.	.2	0.5	0.3	5.2
U. H. K.	.1	0.2	.3	1.1
2335	.1	3.5	.1	2.7
Rupperi	.15	1.2	.5	2.1

[a] In this and following tables "U. R." stands for the unadsorbed residue and "Z_2" for our concentrate, both of which are previously described. The numbers represent the yeast crops expressed in milligrams obtained in eighteen hours. The blank is our synthetic medium unless otherwise indicated.

It will be noted in this experiment that in the cases of Yeast 578, O. P. yeast, and Untergarige Hefe K, there is a marked complementary action of the two preparations. In Gebriide Mayer and Ruppert yeast the effect of the two preparations is approximately additive, while in the case of Yeast *2335* the concentrate seems to have no stimulating effect. (However, in two other experiments this preparation did have a slight stimulating effect on Yeast *2335.)*

In the cases of Yeast *2335* and Gebriide Mayer the unadsorbed residue alone is very effective. Experimenters who might be working with either of these yeasts would naturally conclude that fuller's earth treatment removes practically none of the active substance from an active solution, whereas exactly contrary results are obtained with three other yeasts.

Table II depicts experiments in which were tested, in parallel, the effects of 1-mg. doses each of our unadsorbed residue, Eddy and Kerr's "α-Bios" and "β-Bios." The latter two preparations were kindly furnished by Drs. Eddy and Kerr.

TABLE II

EFFECT OF UNADSORBED RESIDUE, "α-BIOS" AND "β-BIOS" ON SIX YEASTS

Yeast	Blank	1 Mg. of U. R.	1 Mg. of "α-Bios"	1 Mg. of "β-Bios"
578	0.1	0.5	0.1	0.4
G. M.	3.7	6.5	2.9	5.0
O. P.	0.1	0.5	0.1	0.2
U. H. K.	.15	.5	.2	.15
2335	.025	.3	.025	.025
Ruppert	.1	.3	.1	.1

In no case does the "α-Bios" appear to show distinctly stimulating effect on the yeasts when tested in this way. The "β-Bios" shows appreciable stimulation in the case of two yeasts, but in each case an equal dosage of unadsorbed residue gives a greater stimulation. It may be remarked here that Eddy and Kerr have, in their experiments, generally used a longer growth period in which case very *small* amounts of active material may cause very marked increases in the yeast crop. This effect of the longer growth period is shown very clearly in the contrast between the upper and lower curves in Figs. 1 and 2.

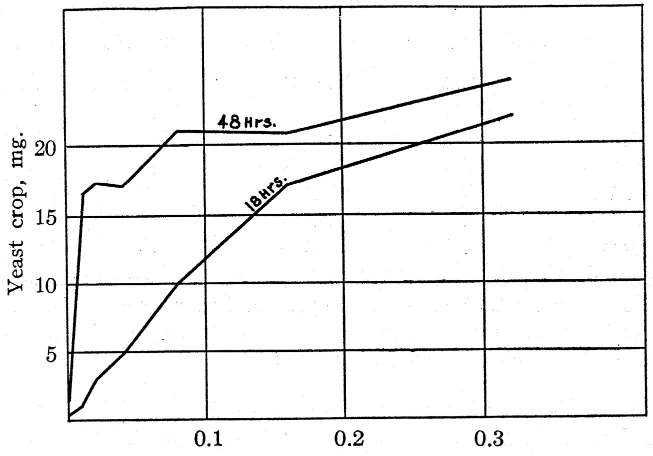

Fig. 1.—Yeast No. 578.

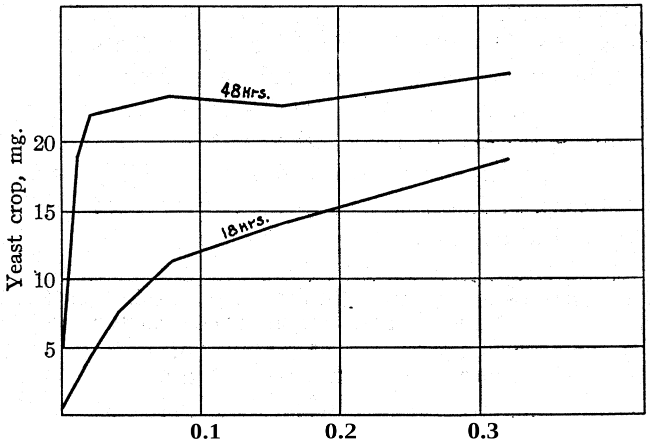

Fig. 2.—Gebriide Mayer.

In Table III are given results of tests of "a-Bios" and "β-Bios" in conjunction with our concentrate, which we have designated as "Z_2." The yeast used in this experiment was No. 578 which, it will be noted in Table I, is very slightly affected by "Z_2" alone. The purpose was to see whether either of these preparations acted as a supplement to the preparation which we obtained from material adsorbed on fuller's earth. Both "α-Bios" and "β-Bios" have been obtained from material which was not adsorbed by fuller's earth. The results of the tests are negative, that is, neither "α-Bios" nor "β-Bios" appears to supplement "Z_2" so far as yeast No. 578 is concerned.

TABLE III

EFFECT OF "α-BIOS" AND "β-BIOS" PLUS "Z_2" ON YEAST 578

Blank	0.4	0.1 mg. of "α-Bios"	0.4
1 mg. of "α-Bios"	.2	0.1 mg. of "α-Bios" +0.005 of Z_2	.4
1 mg. of "α-Bios" +0.005 of Z_2	.3	0.1 mg. of "β-Bios"	.5
1 mg. of "β-Bios"	.4	0.1 mg. of "β-Bios" +0.005 of Z_2	.5
1 mg. of "β-Bios" +0.005 of Z_2	.6		

In the experiment referred to in Table IV, yeast No. 578 was used. The amounts of "Z_2" and unadsorbed residue in the media were each varied separately, with the results indicated. It is apparent that if either component is held at a proper level, variation of the other component causes a variation of yeast crop which is roughly proportional in the lower concentrations to the amount of the preparation added. It is also apparent from the results that a dosage of "Z_2" as low as 0.0006 mg. (0.00005 mg. per cc.) causes marked stimulation in the growth of the yeast. If a langer growth period is used this same dosage will cause a much greater contrast between the crop obtained and that obtained in the control medium. Results of this sort have been obtained repeatedly. In Fig. 1 a case appears in which a dosage which causes approximately a doubling of growth in eighteen hours, causes a 33-fold increase over the blank when the forty-eight hour growths are compared.

TABLE IV

EFFECT OF VARYING "Z_2" AND UNADSORBED RESIDUE (YEAST 578)

Blank (8 mg. of U. R.)	0.6	Blank (0.0024 mg. of Z_2)	0.2
Same + 0.0006 mg. of Z_2	1.4	Same + 1 mg. of U. R.	.5
Same + 0.0012 mg. of Z_2	2.2	Same + 2 mg. of U. R.	.7
Same + 0.0024 mg. of Z_2	3.3	Same + 4 mg. of U. R.	1.8
Same + 0.0048 mg. of Z_2	5.6	Same + 8 mg. of U. R.	3.3
Same + 0.0096 mg. of Z_2	5.5	Same + 16 mg. of U. R.	3.9
Same + 0.096 mg. of Z_2	11.8	Same + 32 mg. of U. R.	4.3

The results of tests of Bios I (Inositol), discovery of which was announced[5] from Lash Miller's laboratory are shown separately in Table V because the other work had been completed before these publications appeared. The inositol used in these experiments was obtained from the Eastman Laboratories. It will be noted that in the doses used the inositol

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[5] *Science Suppl.*, X, July 6, 1928; Eastcott, *J. Phys. Chem.*, 32, 1094 (1928).

has very little effect on the growth of any of the six yeasts either alone or in conjunction with our "Z_2" concentrate.

It may be that our "Z_2" is not the proper supplement to the inositol. However, since "Z_2" does supplement our "unadsorbed residue," inositol is evidently not the active substance in this residue. From the method of preparation of "Z_2" and the very small doses which are effective, it is clear that inositol is not the active material in the "Z_2" concentrate.

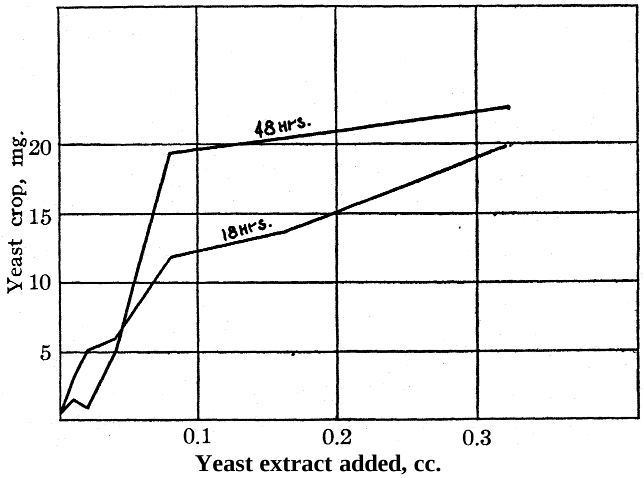

Fig. 3.—Old Process Bakers' Yeast.

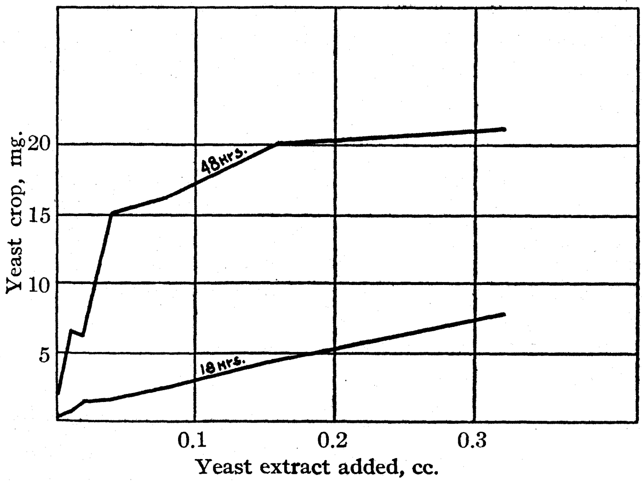

Fig. 4.—Untergärige Hefe K.

The conclusion may be drawn, therefore, that inositol does not constitute the active material in either of the two supplementary fractions which we have found to be, when used together, very stimulatory to the growth of certain yeasts.

An examination of Miss Eastcott's evidence as to the functioning of inositol in yeast growth is not reassuring. We have no reason to doubt the approximate homogeneity of the product which was obtained, but evidence seems to be lacking both as to its potency and constancy. Relatively large doses of inositol were required to cause an effect. A dosage of 0.0033 mg. of inositol per cc. is required to about treble the yeast crop which is obtained in eighteen hours when "Bios II" alone is present. By comparison with our results it may be noted in Table IV that 0.0001 mg. of "Z_2" per cc. (0.0012 mg. per 12 cc.) more than trebles the growth in eighteen hours. Yet our "Z_2" is obviously impure and recent work has indicated that it consists for the most part of inert material.

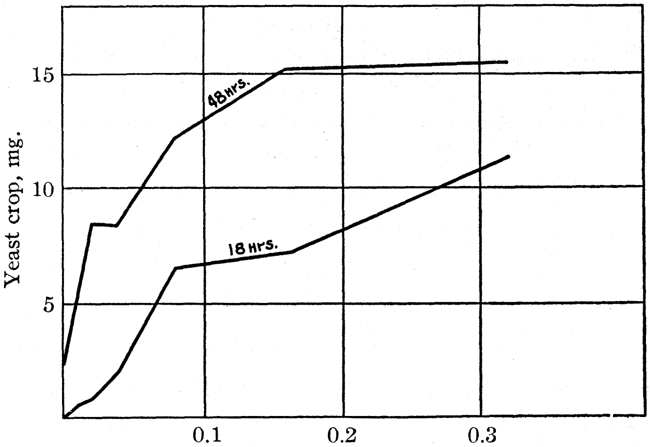

Fig. 5.—Yeast No. **2335.**

As to the constancy of the activity of inositol Miss Eastcott gives no evidence. She states that Kahlbaum's inositol and that obtained from tea showed "no difference" in behavior but no data are given to support the statement. Neither is evidence given nor even a statement made that the activity of the inositol remained constant after recrystallization. In the discussion the question as to the identity of her product with inositol is thoroughly treated but no emphasis is placed upon the question of the identity of her product with the physiologically potent substance for which she was searching.

The inositol that is on the market is obtained from a vegetable source which is probably rich in "bios," and it may be difficult to free the inositol from traces of these impurities. Even when purified on an enormous scale and in a very efficient manner, cane sugar has repeatedly been shown to contain "bios." We have also observed the occurrence of "bios" in highly purified asparagine and Kahlbaum's lactose.

The fact that the yeast crops recorded in Table V are very low as compared with the others is due, we feel sure, to the physiological state of the yeast used. This experiment was made early in the fall after a summer vacation during which the yeast cultures were not transplanted regularly.

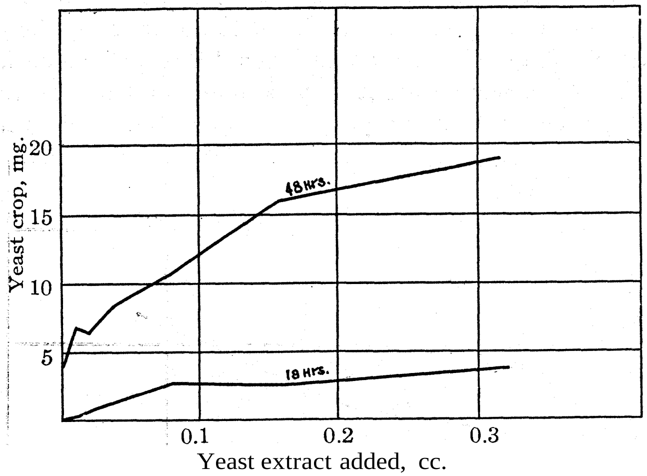

Fig. 6.—Ruppert Brewing Yeast.

After having transplanted the cultures a number of times the growths increased and in a few weeks came back and have remained at the higher level. There is no evidence that these slower-growing cultures of yeast reacted materially differently toward the preparations than the yeast used in the earlier experiments.

TABLE V

EFFECT OF "BIOS I" (INOSITOL) ON SIX YEASTS

		Inositol						
Yeast	Blank	I mg.	0.01 mg.	I mg. +0.0024 mg. of Z_2	0.01 mg. +0.0024 mg. of Z_2	0.0024 mg. of B_2	8 mg. of U. R. +0.0024 mg. of Z_2	8 mg. of U. R.
578	0.05	0.05	0.05	0.1	0.075	0.075	0.7	0.15
G. M.	.4	.4	.4	.4	.4	.4	3.6	3.9
O. P.	.025	.05	.025	.1	.1	.1	0.8	0.15
U. H. K.	.025	.075	.025	.075	.05	.05	0.55	0.45
2335	.025	.025	.025	.025	.025	.025	6.0	4.4
Ruppert	.025	.05	.05	.05	.05	.075	0.7	0.5

Our thanks are due the Research Committee of the University of Oregon for its support of this work and to the Fleischmann Company for the fellowship which they have granted and under which a portion of this work was done.

Summary

1. All six yeasts tested show a very marked stimulation of growth when varying quantities of yeast extracts are added to a synthetic medium,

2. All yeasts fail to show an "optimum" concentration of yeast extract either when an eighteen-hour or a forty-eight-hour growth period is used. That is, in every case the largest crops were obtained when the most extract was added. When toxic materials are present in the extract these results may not be obtained.

3. In the case of most, if not all six, of the yeasts studied it appears that a short growth period (eighteen hours) is much more easily adapted than a longer growth period (forty-eight hours or more) for quantitative studies on yeast nutrilites. If a long growth period is used, a very small dosage of active material may produce an inordinatkly large increase in the yeast crop. The crops are likely to be irregular and there is an unnecessary loss of time. These statements apply primarily to cases in which yeast is grown without agitation.

4. In spite of the uniformities above noted, each of several different strains of yeast (so-called *Saccharomyces cerevisiae*) reacts more or less distinctively toward different "bios" preparations. In some cases the contrast in behavior is very marked. This indicates possible deep-seated differences in the metabolic processes in different strains.

5. The results show that our most concentrated fraction (adsorbable by fuller's earth) in conjunction with the unadsorbed residue stimulates two of the yeasts markedly in very small doses and has a varying-though definite effect on the others. In the case of yeast No. 578, doses of this concentrate as low as 0.00005 mg. per cc. have a marked effect. The same-preparation has little effect on one or two of the yeasts tested and uniformly has little effect on any yeast unless the "unadsorbed residue? is also present. The dosage indicated above is, to the best of our knowledge, much smaller than that used by any other investigators in this field.

6. The effects of "α-Bios" and "β-Bios" and that of inositol on the six yeasts tested are of a lesser order and involve the presence of relatively large amounts of the substances. It seems to us within the realm of possibility that such activities as these preparations possess may be due to occluded or adsorbed impurities.

7. Miss Eastcott's conclusion as to the identity of inositol with a bios (Bios I) does not appear justified by her evidence. Until more convincing proof is offered we must tentatively regard its yeast growth stimulatory effect as probably due to impurities[6]

EUGENE, OREGON

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[6] Miss E. V. Eastcott thanks the Editor for an opportunity to read the manuscript of Williams, Warner and Roehm and to point out that, except in their own paper, the substance to which Mr. Lucas gave the name "Bios I" and which has since been identi-

fied with inactive inosite, has never been spoken of as "a bios." It is one of the constituents into which Lucas separated Wildiers' bios; by itself it has little if any effect on the yeast crop; but if the other constituent, namely, "Bios II," be present in the culture medium, addition of inosite much increases the crop. As to the inosite from tea, Miss Eastcott's paper, *J. Phys. Chem.*, **32**, 1094 (1928), states that it was recrystallized from methyl alcohol and water and obtained in two "clear white" crystalline forms, anhydrous and the dihydrate, both of which were analyzed; also that it made no difference in the yeast crops obtained with various preparations of Bios II whether Kahlbaum's inosite was employed or that from tea. Her laboratory note-books show that the last six recrystallizations had no effect on the "activity" of the latter.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

INTERACTION OF ALKYL SULFIDES AND SALTS OF MERCURY

BY W. F. FARAGHER, J. C. MORRELL AND S. COMAY

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The property of organic sulfides of forming compounds with certain heavy metal salts was discovered by Loir.[1] He prepared compounds of methyl and ethyl sulfides with mercuric chloride, mercuric iodide and platinum chloride.

Some of the results reported by Loir were criticized by subsequent investigators. Blomstrand[2] found the properties of the product formed by the interaction of ethyl sulfide and platinic chloride to be different from those reported by Loir: the melting point was 70° higher. Abel,[3] who discovered ethyl sulfide in dog's urine, contested the originally reported melting point of the compound of ethyl sulfide and mercuric chloride.

Phillips[4] disputed the formula assigned by Loir to the reaction product of methyl sulfide and mercuric chloride. He found that the compound was $3HgCl_2\cdot 2(CH_3)_2S$ and not $(CH_3)_2S\cdot HgCl_2$, as stated by Loir. The reason for the conflict between reports is presented in this paper.

The compounds of alkyl sulfides and salts of platinum were quite extensively investigated by Blomstrand,[2] Blomstrand and his co-workers,[5] Klason[6] and Rây.[7]

On the other hand, the literature contains little information about the compounds of alkyl sulfides and salts of mercury. Smiles[8] reported the preparation of five addition compounds of alkyl sulfides and mercuric iodide: $(CH_3)_2S\cdot HgI_2$, $(CH_3SC_2H_5)\cdot HgI_2$, $(C_2H_5)_2S\cdot HgI_2$, $(C_5H_{11})_2S\cdot HgI_2$ and $(C_6H_5CH_2)_2S\cdot HgI_2$.

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[1] Loir, *Ann.*, **87**, 369 (1853).

[2] Blomstrand, *J. prakt. Chem*, [2] **27**, 190 (1883).

[3] Abel, *Z. physiol. Chem.* (Hoppe-Seyler) **20**, 269 (1895).

[4] Phillips, THIS JOURNAL, **23**, 254 (1901).

[5] Blomstrand and others, *J. prakt. Chem.*, [2] **38**, 353 (1888).

[6] Klason, *Ber.*, **28**, 1493 (1895).

[7] Rây, *Quart. J. Indian Chem. Soc.*, **2**, 178 (1925).

[8] Smiles, *J. Chem. Soc.*, **77**, 163 (1900).

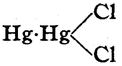
Faragher, Morrell and Monroe[9] found that alkyl and aromatic sulfides react quantitatively with powdered "normal" mercurous nitrate, $Hg_2(NO_3)_2\cdot 2H_2O$. No analysis of the products or description of the reaction was given by them since this problem was outside the scope of their work.

It was first observed in the present work that metallic mercury is formed when an alkyl sulfide reacts with a mercurous salt, e. g., mercurous nitrate. The reaction is shown by the equation

$$2R_2S + Hg_2(NO_3)_2 \longrightarrow (R_2S)_2\cdot Hg(NO_3)_2 + Hg + \text{heat}$$

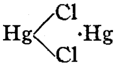
The behavior of ethyl sulfide and other organic sulfides toward the mercurous salts used was found to be analogous to the behavior of pyridine toward mercurous salts. Lang[10] found that metallic mercury is precipitated at once when mercurous nitrate is treated with pyridine. The mercuric nitrate formed reacts with the pyridine to give the compound $(C_5H_5N)_2\cdot Hg(NO_3)_2$. No quantitative results were reported. François[11] investigated quantitatively the action of aniline, phenol and alcohol on mercurous iodide at an elevated temperature and found that the decomposition of mercurous iodide was in each case limited. Lang explains the mechanism of the change by the assumption, "A state of equilibrium exists in the solution of the mercurous salt dissociated partially into mercury and mercuric salt, the number of molecules decomposing and reforming in unit time being equal; but if the equilibrium is destroyed by the removal of the mercuric salt by pyridine, etc., metallic mercury separates."

Werner[12] in discussing the constitution of the mercurous salts considers that Lang's discovery that pyridine rapidly decomposes mercurous chloride into mercury and mercuric chloride is not in accord with the formula for mercurous chloride, Cl–Hg–Hg–Cl. He says: "This behavior of mercurous chloride seems to indicate that it is an addition product of mercury and mercuric chloride, and mercury, like water, is capable of forming addition compounds; the amalgams correspond to the hydrates as was shown in such an excellent way by Forster." Accordingly, Werner proposed either of the following two formulas for mercurous chloride



$$Hg\cdot Hg\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right.$$

and



$$Hg\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right\rangle\cdot Hg$$

Although pyridine reacts rapidly with solid mercurous chloride, ethyl sulfide does not react, and methyl sulfide causes the formation of metallic mercury from mercurous chloride only in the presence of water. It will be shown that it cannot be predicted that because a substance reacts readily with a mercuric salt it will react with the corresponding mercurous salt; the specific reactivity of each of the reacting substances cannot be ignored.

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[9] Faragher, Morrell and Monroe, J. *Ind.* Eng. Chem., 19, 1283 (1927).

[10] Lang, Ber., 21, 1587 (1888).

[11] Franpis, *Compt.* rend., 121, 253, 700, 880 (1895).

[12] Werner, *Z. anorg. Chem.*, 15, 5 (1897).

Usually some members in the series of alkyl sulfides are more reactive than others toward a particular mercurous salt. In some cases the solvent is an important factor. Methyl sulfide, as previously stated, does not react with mercurous chloride unless water is present; but it reacts with mercurous acetate in the absence of water. Ethyl sulfide and the other alkyl sulfides used in this investigation caused mercury to separate from mercurous acetate only in the presence of water. Thiophene does not react with powdered "normal" mercurous nitrate, but if water is added, mercury is precipitated. Methyl sulfide, ethyl sulfide and *iso*-amyl sulfide separate mercury immediately from mercurous sulfate in the absence of water. Although in some of the instances mentioned solubility may be the reason for the fact that the reaction proceeds only in the presence of water, nevertheless in the case of methyl sulfide and mercurous chloride, the compound formed is practically insoluble in water. Therefore, it is apparent that the mechanism of the reaction requires further investigation, especially when one recalls that pyridine separates mercury from solid mercurous chloride immediately and also that the sulfides separate mercury from mercurous iodide in the absence of water.

Experimental

Action of Alkyl Sulfides on Mercurous Salts. **Ethyl Sulfide and $Hg_2(NO_3)_2·2H_2O$.**—Analysis of the products of the interaction of ethyl sulfide and mercurous nitrate showed that the reaction is represented by

$$2Et_2S + Hg_2(NO_3)_2 \longrightarrow (Et_2S)_2·Hg(NO_3)_2 + Hg$$

This was shown as follows: 180 cc. of an 8% aqueous solution of mercurous nitrate (0.5% of nitric acid was added to keep the salt in solution) was treated with 2.27 g. of ethyl sulfide. The metallic mercury that separated weighed 2.51 g. or 99.6% of the theoretical weight.

When ethyl sulfide and powdered normal mercurous nitrate were used in molecular proportions, the amount of mercury weighed was 97 to 98% of the theoretical amount.

The compound, $(Et_2S)_2·Hg(NO_3)_2$, was isolated as follows. The sulfide was dissolved in hexane and treated with normal mercurous nitrate by shaking for five minutes. After standing for a few hours the hexane and the liquid reaction product were decanted from the mercury and the liquid product separated from the hexane. The sirupy reaction product was filtered twice to remove all trace of metallic mercury. The filtrate was placed under a vacuum of two cm. of mercury and after a few hours long white needles appeared. The needles were removed and kept under vacuum again for fifteen hours. They melted to a clear liquid at 63°. The crystals are very hygroscopic and if kept even for a short time in the open they absorb moisture from the air and become pasty.

Analysis of the dry crystals for mercury was made by treating them with a solution of sodium thiosulfate, using in excess of four moles to one mole of mercuric nitrate. The method of analysis was as follows. The weighed sample was added to 15 cc. of an 18% thiosulfate solution and allowed to boil for five to ten minutes. As soon as the addition compound is added even in the cold it dissociates into the organic and inorganic components; the odor of the sulfide is very pronounced. A concentrated solution of sodium sulfide was then added until an almost clear solution was obtained. If red or black mercuric sulfide was still left undissolved, the mixture was boiled until a complete solution was obtained. About 150 cc. of water and some solid ammonium nitrate crystals were added. The mixture was boiled for fifteen minutes and the precipitate collected in a Gooch crucible, washed and dried at 120° in the usual manner This procedure was found to give accurate results when mercuric chloride was treated with sodium thiosulfate solution.

The reaction between solid sodium thiosulfate and mercuric chloride was investigated by Allen and Crenshaw.[13]

The accuracy of the procedure adopted in this work can be seen from the following results: for 0.5000 *g.* of mercuric chloride, theory requires 0 4283 g. of mercuric sulfide. Found: 0.4270 and 4275 g.

When the black precipitate first formed on boiling 0.5000 g. of mercuric chloride with 1.828 g. of the thiosulfate in 15 cc. of water was weighed after washing and drying, the amounts of mercuric sulfide obtained were 0.3885 and 0.3883 g., respectively, approximately only 90% of the theoretical.

The crystals of the addition compound, $(Et_2S)_2{\cdot}Hg(NO_3)_2$, were analyzed for mercury by the procedure just described and the percentage of mercury corresponded within experimental error to that required by the formula given.

Anal. Calcd.: Hg, 39.75. Found: Hg, 39.58, 39.45.

Reaction between Alkyl Sulfides and Mercurous Salts.—The following alkyl sulfides were tested qualitatively for their behavior toward various mercurous salts: methyl sulfide, ethyl sulfide, n-propyl sulfide, n-butyl sulfide, *iso*butyl sulfide and *iso*-amyl sulfide. The results obtained are given briefly.

(1) All alkyl sulfides precipitate mercury from powdered mercurous nitrate, $Hg_2(NO_3)_2{\cdot}2H_2O$, or aqueous solution of mercurous nitrate.

(2) Only methyl sulfide precipitates mercury from mercurous chloride and it does so only in the presence of water. The other alkyl sulfides seem to have no action on this mercurous salt even in the presence of water.

(3) Methyl sulfide precipitates mercury from mercurous acetate even when water is absent. The other sulfides react likewise but only in the presence of water.

(4) All the alkyl sulfides used react with mercurous sulfate even in the absence of water.

(5) All the sulfides precipitate mercury from mercurous iodide. Methyl, ethyl and n-propyl sulfides when used in excess give solutions and metallic mercury. The other sulfides give grayish precipitates which dissolve in benzene with the separation of mercury.

Alkyl Sulfides and Mercuric Salts.—Generally speaking, the addition compounds of alkyl sulfides with salts of oxy-acids are water-soluble compounds. This phenomenon is in agreement with the analogous finding of Blomstrand[2] that the compounds of ethyl sulfide and the platinum salts of oxy-acids (except the nitrite) are water soluble.

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[13] Allen and Crenshaw, *Am. J. Sci.*, [4] **34, 369 (1912).**

Interaction of Alkyl Sulfides and Mercuric Chloride.—Only the first two members in the series of the aliphatic sulfides had been investigated previously. The alkyl sulfides and mercuric chloride were found to give under different conditions two types of addition compounds for each sulfide, the types varying with the sulfide used. It was also found that Types 2 and 3 are in some cases easily converted into each other.

TABLE I

PREPARATION, PROPERTIES AND ANALYTICAL DATA OF ADDITION COMPOUNDS OF ALKYL SULFIDES WITH MERCURIC CHLORIDE

No.	Soln. of $HgCl_2$ in	Alkyl sulfide	Cryst. solvent	M. p., °C.
1	Alcohol	Ethyl sulfide	Alcohol	76.5–77
2	Alcohol	Ethyl sulfide	Bz or acetone	119–119.5
3	Alcohol	n-Propyl sulfide	Alcohol	87.5–88
4	Alcohol	*n*-Propyl sulfide	Benzene	121–122
5	Alcohol	Isobutyl sulfide	Alcohol	116
6	Alcohol	Isobutyl sulfide	Benzene	131
7	Alc. or water	*n*-Butyl sulfide	Benzene	112–113
8	Water	n-Butyl sulfide	......	Liquid
9	Alc. or water	Iso-amyl sulfide	Benzene	......
10	Water	*Iso*-amyl sulfide	......	Liquid

		Analyses					
		Calcd., %		Found, %			
No.	Compound formed	Hg	S	Hg		S	
1	$(C_2H_5)_2S\cdot HgCl_2$[a]	55.47	9.19	54.94	55.09	8.99	9.11
2	$(C_2H_5)_2S\cdot 2HgCl_2$[b]	63.37	5 05	63.03	63.46	5.07	5.23
3	$(n\text{-}C_3H_7)_2S\cdot HgCl_2$[c]	51.48	8.22	50.42	50.65	7.79	
4	$(n\text{-}C_3H_7)_2S\cdot 2HgCl_2$[d]	60 68	4 84	60.41	60.91	4.80	4.85
5	$(iso\text{-}C_4H_9)_2S\cdot HgCl_2$[e]	48.04	..	47.81	47.89	....	
6	$(iso\text{-}C_4H_9)_2S\cdot 2HgCl_2$[f]	58 21	..	58.03	58.29	....	
7	$(n\text{-}C_4H_9)_2S\cdot 2HgCl_2$[g]	58.21	..	58.11	57.92	....	
8	$[(n\text{-}C_4H_9)_2S]_2\cdot HgCl_2$	35.37	..	36.27	36.37	....	
9	$(iso\text{-}C_5H_{11})_2S\cdot 2HgCl_2$[h]	55.93	..	55.81	55.73	....	
10	$[(iso\text{-}C_5H_{11})_2S]_2\cdot HgCl_2$	32.35	..	33.40	33.56	....	

[a] White needles. If a large excess of $HgCl_2$ is used or if the product is recrystallized several times from alcohol, the higher compound, $(C_2H_5)_2S\cdot 2HgCl_2$, is formed. [b] White plates. When the product is recrystallized from alcohol it does not change. [c] Long white needles. Solvent of crystallization is important, while an excess of either of the reactants is of no moment. [d] White plates. When recrystallized from alcohol, the lower compound, $(n\text{-}C_3H_7)_2S\cdot HgCl_2$, is formed. [e] Same as for 3. [f] Same as for 4. [g] White plates. When alcohol is used as the solvent, a large excess of $HgCl_2$ is required in order to get precipitation. In water, molecular proportion of the reactants is sufficient. A clear oily liquid containing compounds 7 and 8 is formed. Addition of ether precipitates the solid. [h] Same as for 7.

Ethyl Sulfide and Mercuric Chloride.--The addition compound obtained by the interaction of ethyl sulfide and mercuric chloride was formerly considered to be an equimolecular compound of the two reacting substances. Abel[3] in disagreeing with the discoverer about the melting point of the reaction product said that Loir did not make a pure compound. Abel found that the melting point of his purified compound, which was recrystallized from alcohol and ether, was 119". Loir had reported a melting point of 90° for his product. Abel assumed that the compound melting at 119° was the same as that made by Loir. No analysis was reported by Abel, although he obtained under some conditions a product melting at 80°.

During the present investigation many experiments were made to find the reason for these discrepancies. As will be shown later, the reason was discovered to be the existence of two compounds of ethyl sulfide and mercuric chloride, $Et_2S\cdot HgCl_2$ and $Et_2S\cdot 2HgCl_2$. The two compounds have widely different melting points. They are obtained in a pure state when the proper conditions of formation as well as of recrystallization are used.

(a) **$Et_2S\cdot HgCl_2$.**—This compound is obtained when ethyl sulfide and mercuric chloride are used in an equimolecular proportion and the product is recrystallized either from absolute alcohol or from acetone containing a small quantity of ethyl sulfide.

When this crystalline compound was recrystallized from ether, a compound melting at 112–119° was obtained. This compound is a mixture of the two addition compounds. This fact explains why Abel obtained the higher-melting product, since he purified his product by recrystallization from ether.

(b) **$Et_2S\cdot 2HgCl_2$.**—This compound may be obtained pure if an excess of mercuric chloride solution is used and the product of the reaction is recrystallized once or twice from acetone or from benzene.

An acetone solution of the crude product obtained as described in section (a) was left partially covered overnight. Both types of crystals were formed. They were separated by hand-picking and were found to melt at 77° and 119.5°, respectively. Crystals of $Et_2S\cdot HgCl_2$ when recrystallized several times from either acetone or benzene are converted into $Et_2S\cdot 2HgCl_2$. The crystals thus obtained were recrystallized several times from absolute alcohol. No conversion was effected; the compound melted at 119.5".

***n*-Propyl** Sulfide and Mercuric Chloride. (a) ***n*-$Pr_2S\cdot HgCl_2$.**—When alcohol is the medium of the reaction, the crude reaction product melts invariably at 85°, even though an excess of the sulfide or of the mercuric salt is used. Also, in both cases the compounds recrystallized from absolute alcohol consist of long white needles melting at 87.5–88°.

(b) ***n*-$Pr_2S\cdot 2HgCl_2$.**—This compound is obtained by recrystallizing *n*-$Pr_2S\cdot HgCl_2$ (a) twice from benzene.

When this compound is recrystallized from alcohol, long needles of *n*-$Pr_2S\cdot HgCl_2$, melting at 87.5–88°, are invariably obtained. Thus the two compounds are convertible into each other.

Isobutyl Sulfide and Mercuric Chloride. (a) *iso*-$Bu_2S\cdot HgCl_2$.—The compound was obtained by the action of isobutyl sulfide on an alcoholic solution of the mercuric salt. The precipitate was very voluminous. Recrystallized from absolute alcohol, the crystals melted at 116° after sintering.

(b) ***iso*-$Bu_2S\cdot 2HgCl_2$.**—The compound was obtained by recrystallizing *iso*-$Bu_2S\cdot HgCl_2$ (a) twice from benzene.

Some of the crystals melting at 131° were recrystallized again from alcohol. The new crystals melted at 116". Analysis gave Hg, 47.79, instead of the theoretical value of 48.04 for *iso*-$Bu_2S\cdot HgCl_2$.

Thus isobutyl sulfide behaves like ethyl sulfide and n-propyl sulfide by forming with mercuric chloride two addition compounds; it is like n-propyl sulfide with respect to the easy conversion of one compound into the other by using different solvents for recrystallization.

***n*-Butyl** Sulfide and Mercuric Chloride.—The interaction of n-butyl sulfide and mercuric chloride yielded two types of addition compounds, one of which had not been made with ethyl, n-propyl and isobutyl sulfides. The compound, $n\text{-Bu}_2\text{S}\cdot\text{HgCl}_2$, seems to be non-existent. When the sulfide and the mercuric salt are used in the molecular proportion of 1:1 in alcohol, no precipitate is formed; but when the reacting substances are taken in the molecular proportion of 2:1, a heavy precipitation of white crystals occurs. However, if water is used as the solvent, a liquid separates when the reacting substances are taken in the molecular proportion of 1:1.[14] This liquid product when treated with a small quantity of ether yields a heavy mass of white crystals which on analysis were found to be the addition compound, $n\text{-Bu}_2\text{S}\cdot2\text{HgCl}_2$. The ether solution, when evaporated, leaves an oily residue which by analysis was found to be the addition compound, $(n\text{-Bu}_2\text{S})_2\cdot\text{HgCl}_2$.

The reactions involved may be explained as follows

$$3\,n\text{-Bu}_2\text{S} + 3\text{HgCl}_2 = \underset{\text{Solution}}{2\,n\text{-Bu}_2\text{S}\cdot1\text{HgCl}_2 + n\text{-Bu}_2\text{S}\cdot2\text{HgCl}_2} \qquad (1)$$

$$\underset{\text{(Soln.)}}{2\,n\text{-Bu}_2\text{S}\cdot1\text{HgCl}_2 + n\text{-Bu}_2\text{S}\cdot2\text{HgCl}_2} \xrightarrow{+\text{ ether}} \underset{\text{(In ether soln.)}}{n\text{-Bu}_2\text{S}\cdot2\text{HgCl}_2 + (n\text{-Bu}_2\text{S})\cdot\text{HgCl}_2} \qquad (2)$$

The compound $n\text{-Bu}_2\text{S}\cdot2\text{HgCl}_2$ is only slightly soluble in ether, while the compound $(n\text{-Bu}_2\text{S})_2\cdot\text{HgCl}_2$ is very soluble in this solvent.

(a) $\boldsymbol{n\text{-Bu}_2\text{S}\cdot2\text{HgCl}_2}$.—This compound was also obtained from 8.5 g. of mercuric chloride and 1.5 g. of n-butyl sulfide, i. e., weights in the proportion of 3 moles of the salt to 1 mole of the sulfide. When only once recrystallized from benzene, the percentage of mercury found was 55.5, but when the product was crystallized again from the same solvent, almost the theoretical value for mercury was found.

(b) $\boldsymbol{(n\text{-Bu}_2\text{S})_2\cdot\text{HgCl}_2}$.—This compound was obtained as previously described. Since Compound (a) is soluble in Compound (b), one would expect to find Compound (a) in Compound (b) as an impurity. On standing for a few days, a white precipitate was observed on the bottom of the test-tube. This change indicates the solubility of (a) in (b) as the cause of the high percentage of mercury.

***Iso*-amyl** Sulfide and Mercuric Chloride.—The addition products obtained by the interaction of iso-amyl sulfide and mercuric chloride are similar in their constitution to those obtained from n-butyl sulfide and the mercuric salt. The method of preparation is also the same.

(a) $\boldsymbol{iso\text{-Am}_2\text{S}\cdot2\text{HgCl}_2}$.—The compound may be obtained either by using an excess of mercuric chloride in alcoholic solution or by using the reacting substances in the molecular proportion of 1:1 in an aqueous medium and then treating the product with ether. The results of analysis of the compound obtained by the latter method are given here.

(b) $\boldsymbol{(iso\text{-Am}_2\text{S})_2\cdot\text{HgCl}_2}$.—This compound was obtained by using the sulfide and the mercuric salt in equimolecular proportion with water as the solvent; the product was then treated with ether. The high percentage of mercury may be explained by the solubility of Compound (a) in Compound (b).

Methyl Sulfide and Mercuric **Chloride.**—Loir[1] assigned to the reaction product of

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[14] n-Propyl sulfide and mercuric chloride in equimolecular proportions in water as solvent yield white crystals. This behavior shows that the reaction is different for n-butyl sulfide and iso-amyl sulfide.

methyl sulfide and mercuric chloride the formula $(CH_3)_2S \cdot HgCl_2$. Phillips[4] reinvestigated the compound and in accordance with the results of his analysis for mercury, sulfur and chlorine, gave to it the formula $2(CH_3)_2S \cdot 3HgCl_2$. The compound has no definite melting point. By heating rapidly, a clear liquid is obtained at 151°. The compound is only sparingly soluble in benzene and practically insoluble in the other ordinary organic solvents. The product obtained from alcoholic mercuric chloride and an equimolecular proportion of methyl sulfide was dissolved in an excess of boiling benzene. The crystals that separated were analyzed for mercury and sulfur.

Anal. Calcd. for $2(CH_3)_2S \cdot 3HgCl_2$: Hg, 64.63; S, 6.42. Found: Hg, 63.28, 62.83; S, 6.78, 6.73.

There is a possibility that the product is a "molecular" compound made up of equimolecular proportions of $Me_2S \cdot HgCl_2$ and $Me_2S \cdot 2HgCl_2$, the two types of addition compounds that were obtained from ethyl, n-propyl and isobutyl sulfide with mercuric chloride. Were it possible to find a favorable solvent, the two types might be separated. An analogous situation was found by Rây[7] for the compound $(Et_2S)_2 \cdot PtCl_3$. On recrystallization from boiling alcohol, he succeeded in obtaining the compounds $(Et_2S)_2 \cdot PtCl_2$ and $(Et_2S)_2 \cdot PtCl_4$ from $2(Et_2S)_2 \cdot PtCl_3$.

Summary

1. The action of alkyl sulfides on mercurous salts was investigated. The reaction was found to be a conversion of the mercurous salt into metallic mercury and the corresponding mercuric salt, and the formation of an addition compound of the alkyl sulfides with the mercuric salt.

2. In some cases the reaction takes place only in the presence of water.

3. Except for methyl sulfide, the alkyl sulfides have no action on mercurous chloride.

4. The addition compounds of alkyl sulfides and mercuric salts of most oxyacids are water soluble.

5. The products of reaction of alkyl sulfides and mercuric chloride were investigated. Three types of addition compounds were found. These types are $(R_2S)_2 \cdot HgCl_2$, $R_2S \cdot HgCl_2$ and $R_2S \cdot 2HgCl_2$. Each of the alkyl sulfides formed two of the types, depending on the solvent used.

6. n-Propyl sulfide and isobutyl sulfide form with mercuric chloride two types of compounds that are easily converted into each other by recrystallization from proper solvents.

CHICAGO, ILLINOIS

[CONTRIBUTION PROM THE CHEMICAL LABORATORY OF THE COLLEGE OP LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE MERCURATION OF AURIN AND ATTEMPTS TO MERCURATE SOME OTHER TRIPHENYLMETHANE DYES

BY FRANK C. WHITMORE AND G. J. LEUCK

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The original purpose of this study was to make organic mercury derivatives of crystal violet with the hope that they might be valuable therapeutically. This aim was not achieved. While dimethylaniline and similar substances are mercurated with the greatest ease, less basic amino compounds are not.[1]

No successful mercuration was obtained with crystal violet, N-phenyl methyl violet or malachite green. A small amount of a dimercurated product was obtained from the base of malachite green. It was too insoluble for further study. On the other hand, pararosaniline was mercurated with relative ease. The product was the acetate of triacetoxymercuri-pararosaniline. It was so insoluble that it could not be changed to the corresponding chloromercuri compound.

It was next decided to mercurate aurin. This process proved to be unusually easy, as was to be expected from the work of Wolvekamp on the corresponding tricarboxylic acid.[2] In the present study modified methods of mercuration were developed which made it possible to obtain products containing one, two or three atoms of mercury by merely modifying the solvent. In a mixture of ethyl acetate and acetic acid the mono-mercury product was obtained. In alcohol solution the chief product was the very insoluble tri-mercury compound. By using a mixture of alcohol and acetic acid and a relative excess of aurin, the di-mercury product was obtained. When the mono-acetoxymercuri-aurin was refluxed alone in alcohol, it was converted to the triacetoxymercuri compound and free aurin.

The explanation of these reactions is that the mercuration reactions are reversible. The use of alcohol removes the acetic acid formed in the mercuration reaction and favors the formation of the very insoluble tri-mercury product. An increase in the acetic acid concentration favors the di-mercury product. With ethyl acetate and acetic acid and no alcohol, the mercuration is made most difficult and only the mono-mercury compound is obtained. Further evidence for this conception is given by the conversion of acetoxymercuri-aurin to the tri-mercury compound by heating in alcohol and to the trichloromercuri-aurin by heating with sodium chloride solution.

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[1] Kharasch and Jacobsohn, THIS JOURNAL, 43, 1894 (1921); Chalkley, *ibid.*, 47, 2055 (1925).

[2] Wolvekamp, U. S. Patent 1,412,440; C. A., 16, 2199 (1922).

All of the organic mercury compounds obtained in this study were split by sodium iodide to give inorganic mercury and sodium hydroxide.[3]

Experimental

Mercuration of **Pararosaniline.**—A solution of 5 g. (0.014 mole) of pararosaniline acetate and 2 g. (0 006 mole) of mercuric acetate in 500 cc. of water containing 1 cc. of acetic acid was refluxed for three hours. The solution then gave no test for inorganic mercury. After addition of 3 g. (0.009 mole) more mercuric acetate the mixture was refluxed for five hours longer. Inorganic mercury was then present. After three more hours of refluxing only organic mercury was present. On cooling the whole mixture set to a thin jelly. This was evaporated to a volume of 200 cc. It was then filtered by suction, a process requiring several days. The residue was dried first at 50° and then at 80°. It was extracted repeatedly with 95% alcohol and dried again. The product was triacetoxymercuripararosaniline acetate.

Anal. Calcd. for $C_{27}H_{27}O_8N_3Hg_3$: Hg, 53.6. Found: Hg, 52.6, 52.5.

It is a dark brown solid very sparingly soluble in water. After thorough drying it is much more difficultly soluble. It is insoluble in other solvents. When refluxed with an excess of aqueous sodium iodide the mercury is removed quantitatively with the formation of sodium mercuric iodide, sodium hydroxide and pararosaniline base.

The preparation of the mercury compound was repeated according to several other sets of conditions without any noticeable change in the results. The products obtained contained the following percentages of mercury: 52.6, 52.7, 53.1.

Attempts to prepare mercury derivatives of pararosaniline containing one or two atoms of mercury were unsuccessful.

Attempted Mercuration of Malachite Green **and** its Base.—This substance was treated with mercuric acetate under a great variety of conditions. The solvents used included various concentrations of ethyl alcohol, acetic acid, ethyl acetate, benzene and mixtures of these. The time of heating varied from a few minutes to ten days. In no case was there any evidence of formation of organic mercury compounds. In all cases considerable amounts of mercury and mercurous compounds were formed, indicating oxidation of the dye. In one run in glacial acetic acid a small amount of dimethylaminobenzophenone, m. p. 93–94°, was obtained. In several cases addition products containing inorganic mercury were obtained.

When the mercuration was repeated at a higher temperature by refluxing the free base of malachite green for twenty hours in n-butyl acetate, oxidation was the only result, all of the mercury being converted to metal.

Attempted Mercuration of Other Basic Triphenylmethane Dyes.—Similar experiments were carried out with crystal violet (N-hexamethyl pararosaniline), N-phenyl methyl violet (N-phenyl-N-pentamethyl pararosaniline). In no case was an organic mercury compound obtained.

Acetoxymercuri-aurin.—A solution of 4.8 g. (0.16 mole) of aurin and 5.7 g. (0.18 mole) of mercuric acetate in 80 cc. of dry alcohol-free ethyl acetate containing 20 cc. of glacial acetic acid was refluxed .with stirring for six hours. No inorganic mercury remained. The precipitate was removed, washed with alcohol and dried.

Anal. Calcd. for $C_{21}H_{16}O_5Hg$: Hg, 36.5. Found: Hg, 35.8, 36.0.

A larger run using 48 g. of aurin, 58 g. of (90%) mercuric acetate, 240 g. of glacial acetic acid and 760 cc. of 90% ethyl acetate gave 83 g. of the acetoxymercuri-aurin (91% of the calculated amount). Analyses gave 36.4 and 36.5% of mercury.

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[3] Whitmore and Middleton, THIS JOURNAL, 43,619 (1921).

If much more than one molecular equivalent of mercuric acetate was used in the above solvent mixture, inorganic mercury remained even after long refluxing.

Acetoxymercuri-aurin is a red powder soluble in alcohol, acetone and alkalies. When refluxed with sodium iodide solution the carbon–mercury linkage is split with the formation of sodium hydroxide.

Diacetoxymercuri-aurin.—A solution of 19.3 g. (0.065 mole) of aurin and 6 g. (0.17 mole) of 90% mercuric acetate in 300 cc. of 95% alcohol and 12 cc. of glacial acetic acid was refluxed for half an hour with stirring. Longer refluxing gave some of the black trimercurated product. Shorter refluxing gave a smaller yield of dimercurated product. The mixture was cooled and filtered. The product was washed with alcohol and dried at 50°. Diacetoxymercuri-aurin is a bright red powder. It is soluble in alcohol, acetone, ethyl acetate and alkalies.

Anal. Calcd. for $C_{23}H_{18}O_7Hg_2$: Hg, 49.7. Found: Hg, 49.9, 49.2, 50.0.

Triacetoxymercuri-aurin.—A solution of 14.5 g. (0.05 mole) of aurin and 32.0 g. (0.1 mole) of mercuric acetate in 300 cc. of 95% alcohol, 50 cc. of water and 15 cc. of acetic acid was refluxed with stirring for fifteen hours. No inorganic mercury remained. The greenish-black precipitate was collected on a filter, washed with alcohol and dried; wt., 22 g. A similar run using mercuric acetate and aurin in the molar ratio of 3:1 gave the same product. Mercury analyses gave 56.2 and 56.4. Triacetoxymercuri-aurin is a black powder somewhat soluble in alcohol, acetic acid and alkalies.

Anal. Calcd. for $C_{25}H_{20}O_9Hg_3$: Hg, 56.5. Found: Hg, 56.9, 56.7.

Conversion **of Acetoxymercuri-aurin** to **Triacetoxymercuri-aurin.**—A mixture of 5 g. of acetoxymercuri-aurin in 100 cc. of 95% alcohol was'refluxed for 24 hrs. The hot mixture was filtered and the red filtrate discarded. The residue was refluxed with 100 cc. more alcohol for twenty-four hours. It was again filtered, giving a yellow filtrate. The residue was washed with alcohol and dried at 90°, the product being triacetoxymercuri-aurin. It was dark red, whereas the product obtained by direct mercuration was black.

Anal. Calcd. for $C_{25}H_{20}O_9Hg_3$: Hg, 56.5. Found: Hg, 56.9, 56.9.

Trichloromercuri-aurin was prepared from the acetate and sodium chloride in alcohol by refluxing for three days.

Anal. Calcd. for $C_{19}H_{11}O_3Cl_3Hg_3$: Hg, 60.5. Found: Hg, 59.7, 60.5, 60.3.

The same product was obtained by refluxing 5 g. of acetoxymercuri-aurin and 3.5 g. of sodium chloride in 150 cc. of alcohol for three days. It gave mercury analyses of 60.0 and 59.8%.

No way was found of making chloromercuri-aurin.

Summary

1. Pararosaniline yields a triacetoxymercuri compound readily. The base of malachite green gives a small yield of a diacetoxymercuri compound.

2. Aurin gives mono-, di- and triacetoxymercuri compounds depending on the solvent used.

Evanston, Illinois

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

MERCURATED TEREPHTHALIC ACID

BY FRANK C. WHITMORE AND LLOYD L. ISENHOUR

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The mercuration of aromatic acids converts them to amphoteric substances of weakly acid properties. The sodium salts and the chlorides are readily hydrolyzed to give the insoluble anhydro-hydroxymercuri aromatic acids. It was thought that a second carboxyl group in the molecule would give stronger acidic properties. Consequently, mercurated terephthalic acid was prepared and studied. The difference between it and mercurated benzoic acid in forming stable salts is very slight. Both are precipitated from sodium carbonate solution by carbon dioxide. In the case of mercurated terephthalic acid, however, a very careful adjustment of concentration is necessary to obtain complete precipitation. No such precaution is mentioned by the workers with mercurated benzoic acid.[1]

Anhydro-hydroxymercuriterephthalic acid seems to be more soluble in sodium acetate solution than does the corresponding anhydro-hydroxymercuribenzoic acid, although no quantitative study has been made.

The most interesting comparison of the two acids is between their n-butyl esters as regards their stability in hot 95% alcohol. Di-n-butyl chloromercuriterephthalate can be crystallized satisfactorily from hot alcohol. n-Butyl chloromercuribenzoate is hydrolyzed to anhydrohydroxymercuribenzoic acid by boiling with 90% alcohol.

Of many methods attempted for mercurating terephthalic acid only two were successful. One was to reflux an aqueous mixture of terephthalic acid, mercuric acetate, acetic acid and sodium acetate. The other was to fuse diethyl terephthalate with mercuric acetate and a trace of acetic acid at 117°. The use of higher temperatures gave large amounts of an unmanageable dimercurated product.

A method of purification applicable to other mercurated aromatic acids was developed. The mercurated acid was converted to the acid chloride and then to the n-butyl ester.[2] The ester of mercurated terephthalic acid was readily crystallized from hot ethyl or n-butyl alcohol. Since the n-butyl ester of the original acid is a liquid and that of the di-mercurated acid is very insoluble, this method of purification was very successful.

The esters of chloromercuribenzoic acid are more easily hydrolyzed and so must be crystallized from absolute alcohol.

The structure of the mercurated terephthalic acid was determined by conversion to the following mercurated derivatives, the anhydro com-

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[1] Pesci, *Atti Accad. Lincei*, **[5] 9,** *I*, **255 (1899);** Dimroth, *Ber.*, **31,** 2154 **(1898); 32,758 (1899); 35,2032,2853 (1902).**

[2] Whitmore and Middleton, THIS JOURNAL, 44, 1546 **(1922).**

pound, the di-n-butyl ester, the amide and the anilide, and by replacing the mercury by bromine to form 2-bromoterephthalic acid.

The positions of the mercury atoms in the di-mercurated terephthalic acid have not been determined.

Experimental Part

Preparation of Terephthalic Acid. 1. From Commercial Xylene.—Xylene was oxidized by alkaline potassium permanganate. Isophthalic and terephthalic acids were precipitated. They were then dissolved in ammonium hydroxide and the very insoluble barium terephthalate was precipitated and then converted to the free acid; yield, 150 cc. of acid from 600 cc. of crude xylene.

2. From Commercial Cymene.—The oxidation was carried out with dilute nitric acid to give *p*-toluic acid, which was converted to terephthalic acid by alkaline permanganate.

Mercuration of Terephthalic Acid.—A solution of 34 g. (0.2 mole) of terephthalic acid in a slight excess of sodium hydroxide was mixed with a solution of 44.7 g. (0.2 mole) of mercuric oxide in a slight excess of acetic acid and 10 g. of sodium acetate and refluxed for 240 hours. At that time the mixture gave no test for inorganic mercury and was completely soluble in sodium hydroxide solution. The precipitated material was filtered off, washed and dried; wt., 102 g. The filtrate on acidification gave 10 g. of unchanged terephthalic acid. The mercurated product was digested for one hour with 1 liter of concentrated ammonium hydroxide solution and 500 cc. of water. The insoluble material was filtered off and extracted again in a similar way. The two extracts were barely acidified with acetic acid. The white precipitate was collected on a filter, transferred to a large beaker and dissolved in a very slight excess of hot saturated sodium carbonate solution. The solution was filtered from a small amount of insoluble material, cooled and treated with carbon dioxide to precipitate a mixture of the mono-mercurated acid and a little of the di-mercurated product. The mixture was digested for about one hour with 500 cc. of saturated (20°) sodium acetate solution and 1 liter of water. This treatment dissolved the mono-mercury compound. The filtrate was acidified with 40 cc. of glacial acetic acid, filtered, washed with water and alcohol and dried in *vacuo* over phosphorus pentoxide; yield of pure anhydro-2-hydroxymercuri-terephthalate, 18 g. More of the product was obtained from the various residues and mother liquors.

Anal. Calcd. for $C_8H_4O_4Hg$: Hg, 55.0. Found: Hg, 54.5.

Mercuration of Diethyl Terephthalate.—A mixture of 40 g. (0.18 mole) of diethyl terephthalate, 57.5 g. (0.18 mole) of mercuric acetate and 2 cc of glacial acetic acid was heated for seventy hours at 117° (bath of boiling n-butyl alcohol). No test for inorganic mercury was then given. The pasty mass was then steam distilled for twenty-four hours. The residue was digested with ammonium hydroxide solution, filtered and acidified. The mercurated terephthalic acid was purified as before.

Di-n-butyl 2-Chloromercuriterephthalate.—A suspension of 5 g. of the anhydro compound in 200 cc. of chloroform was treated with 20 g. of phosphorus pentachloride. Some heat was evolved. After refluxing for half an hour solution was almost complete. A slight residue was removed by filtration and the filtrate was evaporated on a water-bath to 50 cc. in *vacuo.* It was cooled in ice. The acid chloride separated in crystalline form but it was not possible to prepare it in definite purity for analysis. In its crude state it was heated with 25 cc. of anhydrous n-butyl alcohol. On cooling, fine white crystals of the ester separated. It was crystallized from 15 cc. of hot 95% alcohol and dried in *vacuo* over phosphorus pentoxide; m. p. 82–85°; yield, 70%.

Anal. Calcd. for $C_{16}H_{21}O_4ClHg$: Hg, 39.1. Found: Hg, 39.7.

2-Chloromercuriterephthalamide.—A solution of 2 g. of the ester in 300 cc. of 95% alcohol was treated with dry ammonia gas and allowed to stand for two days. The white precipitate was collected and dried at 100°; wt., 1 g. It did not melt at 300°. Analyses of several samples gave consistently 48.0 ± 0.2 for the mercury content instead of the calculated 50.1. This mercury content corresponds to a monohydrate but no water was given off even at 200°.

The amide was prepared from the crude acid chloride and dry ammonia in chloroform. It was dried in *vacuo* at 140°; yield, 90%.

Anal. Calcd. for $C_8H_7O_2N_2ClHg$: Hg, 50.1. Found: Hg, 40.5.

Anilide of 2-Chloromercuriterephthalic Acid.—The crude acid chloride from 10 g. of the anhydro compound was heated with 50 cc. of aniline. The extract was evaporated in *vacuo* to 5 cc. and treated with 10 cc. of alcohol and 400 cc. of water. The anilide was a brown, amorphous product, somewhat soluble in hot water and readily soluble in hot alcohol. It did not melt at 300°.

Anal. Calcd. for $C_{20}H_{15}O_2N_2ClHg$: Hg, 36.4. Found: Hg, 36.3.

Treatment of the Mercurated Terephthalic Acid with Bromine.—A suspension of 10 g. of the anhydro compound was treated with a solution containing 10 g. of sodium bromide and 1.5 cc. of bromine. The bromine was decolorized at once. The mixture was acidified with hydrochloric acid and the resulting precipitate crystallized from hot alcohol. It showed the properties of 2-bromoterephthalic acid and melted at 299°. Its molecular weight in alcohol as determined by the McCoy method was 269 (calcd. 245).

Purification of Anhydro-2-hydroxymercuribenzoic Acid.—A sample of the crude product containing 62.5% of mercury was converted to the acid chloride and then to the n-butyl ester. This was crystaliized from absolute alcohol. It was then hydrolyzed by boiling with 90% alcohol.

Anal. Calcd. for $C_7H_4O_2Hg$: Hg, 56.1. Found: Hg, 55.8, 55.9.

Summary

1. Terephthalic acid has been mercurated in the 2-position.
2. The salts of the mercurated terephthalic acid are only slightly less hydrolyzed than those of mercurated benzoic acid.
3. A method has been developed for purifying mercurated aromatic acids.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE POLARIMETRIC SECTION, BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XX. TWO ISOMERIC CRYSTALLINE COMPOUNDS OF d-MANNOSE WITH CALCIUM CHLORIDE[1]

BY J. K. DALE[2]

RECEIVED MARCH 8, 1929 PUBLISHED SEPTEMBER 5, 1929

Crystalline compounds of the sugars with inorganic salts, a number of which are known,[3] have hitherto been of little interest in the advancement of our knowledge concerning the structures of the sugars. However, the important position which mannose holds in relation to structural studies makes the preparation and study of any of its compounds or derivatives of unusual interest. Dr. C. S. Hudson informed the author that he had observed the formation of crystals in a solution of mannose and calcium chloride and suggested that the writer prepare and investigate the compound whose existence in a crystalline state had been thus indicated. This proposal led to far more interesting results than had been anticipated. The double compound of mannose and calcium chloride which was obtained showed mutarotation, but the course of the mutarotation was of an unusual character differing from that of any known sugar. Secondly, by evaporating an alcoholic solution on a water-bath the compound was transformed into a second modification, isomeric with the original. Subsequently it was found that either isomer could be made at will from mannose and calcium chloride, or even directly from hydrolyzed vegetable ivory, depending upon the solvent and the temperature at which crystallization took place. The first isomer crystallizes from a concentrated aqueous solution of mannose and calcium chloride at room temperature while the second crystallizes from an alcoholic solution during evaporation on a boiling water-bath. The isomer crystallizing from water at room temperature showed a calcium and chlorine content, loss of weight on drying and specific rotation at equilibrium corresponding to the formula $C_6H_{12}O_6 \cdot CaCl_2 \cdot 4H_2O$. As its initial specific rotation and course of mutarotation, in the early stages at least, do not permit a correlation with either of the known forms of mannose, it will subsequently simply be designated as the "First Isomer." The second isomer, crystallizing from alcohol at the temperature of a boiling water-bath, showed a

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[1] Published by permission of the Director of the Bureau of Standards, U. S. Department of Commerce. By arrangement with Dr. C. S. Hudson this article is included in his series entitled "Relations between Rotatory Power and Structure in the Sugar Group" as Number XX. Number XIX was published by Hudson and Isbell in THIS JOURNAL, 51,2225 (1929).

[2] National Research Fellow.

[3] v. Lippmann, "Chemie der Zuckerarten," 3d ed., pp. 549 and 884.

calcium and chlorine content and specific rotation at equilibrium corresponding to the formula $C_6H_{12}O_6\cdot CaCl_2\cdot 2H_2O$. Its initial specific rotation and course of mutarotation definitely correlate it with β-mannose of initial $[\alpha]_D$ −17°; hence it will be designated as β-mannose$\cdot CaCl_2\cdot 2H_2O$.

Initial Specific Rotation and Mutarotation of the First Isomer, Mannose$\cdot CaCl_2\cdot 4H_2O$.—The first observations of the direction of the mutarotation of this compound indicated that the optically active component was α-mannose. However, an extrapolation of its mutarotation curve to zero time showed an initial specific rotation, calculated to a mannose basis, of $[\alpha]_D$ 4-20', whereas Levene[4] had found $[\alpha]_D$ +30° for a-mannose. Subsequent attempts to obtain readings more quickly after making the

TABLE I

MUTAROTATION OF THE FIRST ISOMER, *d*-MANNOSE$\cdot CaCl_2\cdot 4H_2O$, IN WATER

1.7437 g. of comp. in 25 cc. of soln.; tube length, 2 dm.; $T = 20 \pm 0.5''$

Time after making soln., minutes	$[\alpha]_D^{20}$ of compound	Time after making soln., minutes	$[\alpha]_D^{20}$ of compound		Time	$k_1 + k_2 = \frac{1}{T}\log\frac{r_0 - r_\infty}{r - r_\infty}$	
1.5	−6.22	8	+9.46	→	0	. . .	
3	+4.73	10	+9.08		2	0.032	
4	+7.21	12	+8.95		4	.022	
5	+8.74	14.5	+8.64		6.5	.024	
6	+9.20	17	+8.33		9	.026	Av. 0.025
7	+9.46	22	+7.80		12	.028	
		29	+7.71		21	.021	
		39	+7.09		31	.028	
			+6.72				

TABLE II

OBSERVATIONS

2.856 g. of compound in 25 cc. of soln.; tube length, 2 dm.; T = 2 ± 0.5°

Time after making soln., minutes	$[\alpha]_D^{20}$ of compound	Time after making soln., minutes	$[\alpha]_D^{20}$ of compound		Time	$k_1 + k_2 = \frac{1}{T}\log\frac{r_0 - r_\infty}{r - r_\infty}$	
0.75	−23.68	10.25	+ 6.68				
1.25	− 1760	12	+ 8.62				
1.5	−15.97	15	+10.50				
2	−12.75	18	+11.05				
225	− 1183	23	+11.35	→	0	. . .	
3	− 9.10	30.5	+10.93		7.5	0.0052	
3.5	− 7.89	40	+10.42		17	.0054	
4	− 5.46	50	+10.00		27	.0053	
4.5	− 4.55	63	+ 9 42		40	.0054	
5	− 2.73	79	+ 9.10		56	.0048	Av. 0.0052
5.5	− 1.82	93	+ 8 62		70	.0051	
6	+ 0.61	111	+ 7.71		88	[.0068]	
6.75	+ 1.82	130	+ 7.10		107	[.0085]	
7.5	+ 3.03	147	+ 6.68		124	[.0115]	
8.25	+ 4.85	∞	+ 6.50		∞	. . .	
9	+ 5 16						

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[4] Levene, *J. Biol. Chem.*, 57, 329 (1923); **59**, 129 (1924).

solution gave the unexpected result that the anticipated normal mutarotation was preceded by an extremely rapid change from a negative value, far below even that of β-mannose, to a positive maximum. From this maximum the rotation fell at a rate comparable with that of a-mannose. At 20° in aqueous solution the initial change was too rapid to be measured accurately. At 2" it was still rapid but could be followed with sufficient precision to permit a close estimation of the initial value. In Tables I and II are recorded the mutarotation data for this compound in aqueous solution at the temperatures of 20 and 2°, respectively. The curves A and B of the figure are plotted from these readings.

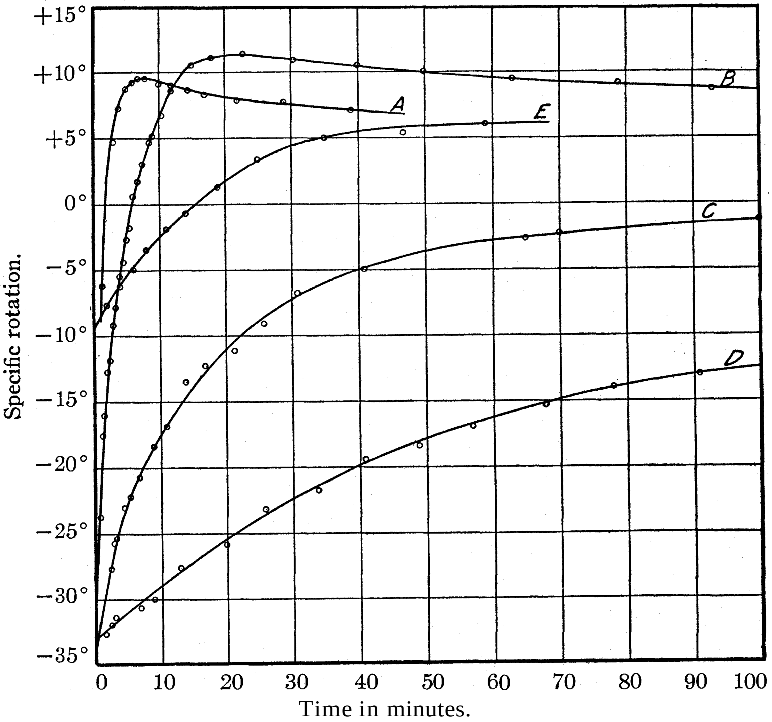

Fig. 1.—Initial stages in the mutarotation of mannose-calcium chloride compounds. Curve **A**, first isomer in water at 20°; Curve B, first isomer in water at 2°; Curve C, first isomer in methanol at 20°; Curve D, first isomer in methanol at 5°; Curve E, beta isomer in water at 20".

The later part of the mutarotation, decreasing from the maximum to an equilibrium value, appears to be unimolecular and the constant found at 20°, $k_1 + k_2 = 0.025$, is of the same order of magnitude as that given by Hudson and Sawyer for β-mannose[5] (0.019), and Levene[4] has shown that a-mannose has the same rate of mutarotation as the β-form. Fur-

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[5] Hudson and Sawyer, THIS JOURNAL, **39**, 475 (1917).

thermore, if this portion of the curve is extrapolated to zero time, the initial specific rotation thus estimated is not far removed from that of a-mannose. These facts constitute evidence that this stage of the mutarotation is the passing of a-mannose to the equilibrium state of mannose solutions.

The initial rapid increase in rotation deserves special attention. The possibility exists that this change is due to a dissociation of the mannose–calcium chloride compound. This explanation appears unlikely, however, because no change in polarization due to a slow dissociation of sugar and salt has been observed in other compounds of this nature.[6] *It appears to be more likely that this change is due to a rapid rearrangement of a new form of mannose to the alpha modification.* If this is true the initial specific rotation of this new form of mannose becomes of special interest. Extrapolation of the mutarotation curve, B, to zero time shows the initial specific rotation of this compound to be about $-30°$, and hence for the mannose constituent, $[\alpha]_D$ $-60°$. Owing to the extreme rapidity of the early stages of the polarimetric change this figure is uncertain by several degrees.

The rate of the polarimetric change of the First Isomer in methanol is much slower than in water; hence in this solvent the course of the change could be followed with more precision and the initial specific rotation determined with more accuracy. Curves C and D show the early stages of the mutarotation of this compound at the temperatures of 20 and 5°, respectively. Extrapolation of these curves to zero time gives the values for the initial specific rotation at these two temperatures as -34 and $-33°$, and hence for the mannose constituent, $[\alpha]_D$ -68.6 and $-66.5°$. The final or equilibrium value for the specific rotation in this solvent was found to be $+4.0$ and $+4.8°$, an average of $+4.4°$, which calculated to a mannose basis equals $+8.9$".

C. S. Hudson[7] has produced evidence from theoretical considerations based upon the principle of optical superposition that the two known crystalline forms of mannose are not a true alpha and beta pair having the same ring structure, but that the form with an initial specific rotation of $+30°$ is the alpha form of a 1,5-ring structure, while the form showing $[\alpha]_D$ $-17°$ is the beta form of a 1,4-ring structure. He has further calculated the specific rotations to be expected for the missing members of these two-ring structures and predicts the value for the β-form of the 1,5-ring structure to be $-65°$ in water solution. The initial specific rotation of a new form of mannose, occurring as a crystalline double com-

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[6] The author has prepared in crystalline form calcium chloride compounds of arabinose, xylose and fructose and also the well-known compound of sodium chloride and glucose. Each of these substances shows a normal mutarotation comparable with that of the sugar constituent. The data will be published in a subsequent article.

[7] C. S. Hudson, THIS JOURNAL, 48, 1425, 1434 (1926).

pound with calcium chloride is here shown to be not far from −60" in aqueous solution. The close agreement of this measured initial specific rotation of the new form of mannose with one of Hudson's calculated values, −65°, lends strong experimental support to his view that the well-known crystalline forms of mannose possess different ring structures, and as a corollary it follows that *the mannose constituent of the crystalline compound here described is the beta form of the sugar corresponding in ring structure with alpha mannose of initial specific rotation* +30°. If this view is correct, the initial mutarotation must be explained as a rapid conversion of the beta form of one ring structure to the corresponding alpha form. The subsequent slower polarimetric change must then be considered to be an establishment of equilibrium between forms of different ring structures.

Mutarotation of β-Mannose·$CaCl_2 \cdot 2H_2O$.—This compound, which was first obtained by concentrating an alcoholic solution of the First Isomer on a boiling water-bath, was characterized by a normal mutarotation in aqueous solution as shown in Table III and by Curve E. The mutarotation constant, $k_1 + k_2$, at 20° was found to be 0.024, a value essentially the same as the constant found for the latter stage of the mutarotation of the First Isomer (0.025) and slightly higher than the value, 0.019, found for β-mannose[5] at this temperature.[8] The final specific rotation, +6.73°, and

TABLE III

MUTAROTATION OF α-MANNOSE·$CaCl_2 \cdot 2H_2O$ IN WATER

3.0146 g. of compound in 25 cc. of soln.; tube length, 2 dm.; T = 20 ± 0.5°

Time after making soln., minutes	$[\alpha]^{20}_D$ of compound	Time	kt + k_2	
2	−7.70	0	..	
4	−6.33	2	0.022	
6	−5.02	4	.025	
8	−3.47	6	.025	
11	−1.97	9	.024	
14	−0.68	12	.024	
19	+1.20	17	.024	Av. 0.024
25	+3.30	23	.027	
35	+4.93	33	.027	
47	+5.35	45	.022	
59	+5.97	57	.023	
∞	+6.73	∞	..	

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[8] The difference between the value $k_1 + k_2 = 0.024$ found for β-mannose·$CaCl_2 \cdot 2H_2O$ and the value $k_1 + k_2 = 0.019$ found by Hudson and Sawyer for β-mannose is too great to be attributed to experimental error. It is more likely that the rate of mutarotation of the mannose constituent of β-mannose·$CaCl_2 \cdot 2H_2O$ is accelerated by the presence of $CaCl_2$ in the solution. In confirmation a mutarotation experiment was made upon β-mannose dissolved in water and a second one upon β-mannose dissolved in a $CaCl_2$ solution of such strength that mannose and $CaCl_2$ were present in equimolecular proportions. Mannose in water alone showed $k_1 + k_2 = 0.020$, while in the $CaCl_2$ solution it showed $k_1 + k_2 = 0.025$.

the extrapolated initial specific rotation, −9.0°, correspond to +12.2° and −16.2°, respectively, for the mannose constituent. Thus this isomer is apparently a compound of $CaCl_2$ with the well known β-mannose of $[\alpha]_D$ −17°.

Acetylation of the Mannose·$CaCl_2$ Compounds.—β-Mannose·$CaCl_2$·$2H_2O$ may be of utility in the synthesis of mannose derivatives because it can be directly acetylated to give a good yield of β-mannose penta-acetate. This may be of timely importance, for pure β-mannose has recently become difficult to obtain, at least in some laboratories. Levene[4] states that after having once prepared a-mannose, subsequent recrystallizations of impure mannose from alcohol invariably gave this form. The author recrystallized at intervals several lots of impure mannose in the research laboratory of St. Andrews University. At first β-mannose was obtained, but unexpectedly one lot appeared as the alpha isomer and thereafter the recrystallized product always consisted of this form. It is true that alpha mannose can be acetylated[9] to give alpha mannose penta-acetate, but the yield is not more than 20% of the theoretical, which is far from satisfactory. On the other hand, 0-mannose or β-mannose·$CaCl_2$·$2H_2O$ readily yields on acetylation 60% or more of the theoretical. The First Isomer (mannose·$CaCl_2$·$4H_2O$) on acetylation with acetic anhydride and pyridine in an ice-bath gave a sirupy gum which after long standing in an ice chest yielded only a few crystals of β-mannose penta-acetate.

Experimental

Preparation of **the** First Isomer, Mannose·$CaCl_2$·$4H_2O$, from **β-*d*-Mannose.**—Twenty g. of β-mannose and 32 g. of crystallized calcium chloride dihydrate were dissolved on a boiling water-bath in 28 cc. of water. On standing overnight at room temperature the solution crystallized to a solid mass. This was thinned out with absolute alcohol, filtered on a Biichner funnel and washed with absolute alcohol. Dried at 35°, the yield was 28 g. It was recrystallized by slow evaporation of a concentrated aqueous solution in a desiccator. A solution of 25 g. of the compound in 25 cc. of cold water was filtered through an asbestos mat, followed by the addition of 10 *cc.* of water. The filtrate was placed in a crystallizing dish in a vacuum desiccator over sulfuric acid. After two weeks this solution had crystallized to a solid mass. It was triturated with absolute alcohol, filtered on a suction filter and washed with a further quantity of alcohol. Dried at 35°, the yield was about two-thirds of the original material. It was readily soluble in water, methanol and hot absolute alcohol. It dissolved slowly in cold 95% alcohol and in acetone. It melted at 101–102° corr.

Analysis.—Chlorine and calcium were determined directly in an aqueous solution of the compound. Moisture was determined by drying at 50 mm. over phosphorus pentoxide, first for six hours at 76°, then for nineteen hours at 100°. Four hours' additional drying at 110° caused no further loss in weight. Subs., 1.0197: AgCl, 0.8080. Subs., 1.0239: CaO, 0.1615. Calcd. for mannose·$CaCl_2$·$4H_2O$: Cl, 19.56; Ca, 11.02; H_2O, 19.80; $[\alpha]^{20}_D$, 6.94". Found: Cl, 19.62; Ca, 11.16; loss on drying to constant weight, 19.10; observed $[\alpha]^{20}_D$, + 6.72".

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[9] Levene, *J. Biol. Chem.*, 57,329 (1923).

Preparation of the First Isomer, Mannose$\cdot CaCl_2\cdot 4H_2O$, from Vegetable Ivory.—A mannose sirup was prepared essentially according to the methods of Hudson and Sawyer[5] and Clark[10] though with a somewhat simplified procedure. One hundred grams of vegetable ivory meal sifted through a 48-mesh sieve was slowly added to 125 g. of 85% sulfuric acid and kneaded into a thick paste. After standing at room temperature for twenty-four hours the paste, which had by this time become liquid, was diluted to a volume of 2 liters and boiled under a reflux condenser for 3 hours, or until samples which were taken at one-half hour intervals showed a constant rotation. The dark red liquor was decolorized with 20 g. of active carbon and neutralized to Congo Red paper by slowly adding freshly precipitated, well washed barium carbonate to the boiling solution. The precipitated barium sulfate was separated by filtration with suction and well washed. The mixed filtrate and washings were acidified with 2 cc. of 5% sulfuric acid and the slight precipitate thus produced was filtered off with the addition of a further 10 g. of decolorizing carbon. This colorless liquor was evaporated to a sirup of about 90% solids as determined with a refractometer. To this sirup, while still warm, there was added a solution of 95 g. of calcium chloride dihydrate in 60 cc. of water. The mixture was stirred to a uniform solution, which was then diluted with 135 cc. of equal parts of absolute alcohol and acetone. Crystallization began almost immediately after cooling and seeding. After one night at room temperature and twenty-four hours in an ice chest, the crystals were filtered off on a Büchner funnel and washed with 400 cc. of equal parts of absolute alcohol and acetone. Dried at 35°, there was obtained 114 g. The melting point, analysis and polarization data identified this product with the First Isomer, Mannose$\cdot CaCl_2\cdot 4H_2O$, as originally obtained from crystalline 0-mannose.

Transformation of the First Isomer, Mannose$\cdot CaCl_2\cdot 4H_2O$, into β-Mannose$\cdot CaCl_2\cdot 2H_2O$.—Ten grams of the First Isomer was dissolved in 40 cc. of hot absolute alcohol and the solution was placed on a boiling water-bath. When the volume had been reduced by about one-quarter, crystals appeared. By the time the volume had been further reduced to about one-half, the solution was well filled with crystals. It was then set aside at room temperature overnight, filtered and the crystals washed with absolute alcohol. Dried at 35° there was obtained 6.5 g. The product was markedly different from the First Isomer. The crystals were well-defined, hard, triangular prisms. They were readily soluble in water and in methanol, only slightly so in cold 95% alcohol and practically insoluble in absolute alcohol. The substance melted at 159–160° (corr.) with decomposition.

Analysis.—Chlorine and calcium were determined directly in aqueous solution. The results agree with the percentages calculated for mannose$\cdot CaCl_2\cdot 2H_2O$, but holding at 50 mm. over phosphorus pentoxide at 100° for five hours caused no loss in weight.

Subs., 0.9799: AgCl, 0.8550. Subs., 1.0168: CaO, 0.1741. Calcd. for mannose$\cdot CaCl_2\cdot 2H_2O$: Cl, 21.71; Ca, 12.23; $[\alpha]^{20}_{D}$, 7.7°. Found: Cl, 21.59; Ca, 12.23; obs. $[\alpha]^{20}_{D}$, 6.73°.

Reversal of the above Transformation.—Ten grams of β-mannose$\cdot CaCl_2\cdot 2H_2O$ was dissolved in 150 cc. of boiling absolute alcohol. The solution was cooled and 1.1 cc. of water was added, just sufficient to make up the deficiency between a dihydrate and a tetrahydrate. The solution was evaporated at room temperature in a current of air to a thin sirup, then seeded with crystals of the First Isomer and placed in a desiccator. After a few days the sirup had crystallized to a semi-solid mass. After filtering, washing with absolute alcohol and drying at 35°, there was obtained 6 g. The melting point and course of mutarotation identified it as the First Isomer.

Preparation of β-Mannose$\cdot CaCl_2\cdot 2H_2O$ from β-Mannose or Directly from Vegetable Ivory.—This compound, though first prepared by transformation of the First Isomer as described above, was subsequently obtained both from crystalline β-mannose and

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[10] Clark, J. *Biol. Chem.*, 51, 1 (1922).

from hydrolyzed vegetable ivory. In the former case 20 g. of β-mannose with 24 g. of calcium chloride dihydrate was dissolved in 12 cc. of hot water, the solution placed on a boiling water-bath, and 80 cc. of hot absolute alcohol slowly added. After remaining on the bath for one-half hour, the solution was well filled with crystals. It was cooled slowly and kept at room temperature overnight. Filtered, washed with 95% alcohol and dried at 35°, there was obtained 28 g.

The same procedure of crystallizing from strong, hot alcohol was applied to the preparation of this compound directly from an impure mannose sirup. Ten g. of a thick sirup from hydrolyzed vegetable ivory prepared as described earlier was mixed with 10 g. of $CaCl_2 \cdot 2H_2O$, previously dissolved in 3 cc. of water, on a boiling water-bath. Thirty-five cc. of warm absolute alcohol was added and the resulting solution kept on the bath until its volume had been reduced by about one-half, when a few crystals of β-mannose·$CaCl_2 \cdot 2H_2O$ were added as seed. Crystallization of the characteristic triangular prisms was soon in evidence and progressed rapidly. After a further short period on the bath and forty-eight hours at room temperature, the crystals were separated on a Biichner funnel, washed with 95% alcohol and dried at 35°. The yield was 8.5 g.

Acetylation of β-Mannose·$CaCl_2 \cdot 2H_2O$.—Ten g. of β-mannose·$CaCl_2 \cdot 2H_2O$ was added in small portions during the course of one-half hour to a mixture of 50 cc. of acetic anhydride and 65 cc. of pyridine, previously cooled in an ice-bath. The mixture was held in the ice-bath with frequent shaking for four hours and then kept in an ice chest for two days. When it was poured onto crushed ice, crystallization of β-mannose penta-acetate took place almost immediately. The crystals were filtered on a suction funnel, washed with water and dried at 35". The yield of this impure material was 5.5 g. The filtrate, after neutralizing with sodium bicarbonate and extracting with chloroform, gave a further 1.25 g. These two quantities of impure crystals were mixed and recrystallized from alcohol, yielding 6 g. of pure p-mannose penta-acetate, or 50% of the theoretical.

Summary

Two crystalline isomeric double compounds of d-mannose with calcium chloride have been prepared.

One, designated the First Isomer, shows an unusual course of mutarotation and an initial specific rotation which indicate that the sugar constituent of the double compound is a new form of mannose.

The extrapolated initial rotation of this compound shows a value for the mannose portion in good agreement with that previously calculated by Hudson for a 0-mannose of 1,5-ring structure.

A second isomer was obtained by evaporating an alcoholic solution of the first on a water-bath. This product is a double compound of the previously known 0-mannose and calcium chloride.

The preparation and study of compounds of the sugars with salts appear to offer a promising method for the discovery of new crystalline forms of the sugars.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

X-RAY INVESTIGATIONS OF OPTICALLY ACTIVE COMPOUNDS

I. A PROOF OF MOLECULAR ASYMMETRY IN OPTICALLY ACTIVE PHENYLAMINOACETIC ACID[1]

BY GEORGE L. CLARK AND G. ROBERT YOHE

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Introduction

An investigation for the purpose of establishing the identity of the d- and l-forms of a substance capable of being resolved into these optically active antipodes, for the purpose of checking up on the similarity of the active and racemic modifications, and for the purpose of finding out whether, after all, the molecules of an optically active substance are asymmetric as first pictured by Pasteur in 1860, and by Le Bel and van't Hoff in 1874, may at first thought seem futile, since the theories concerning these things are so well established. But, as Stewart[2] says: "—— this state of affairs is not altogether healthy since it tends to repel original minds who find little interest in a subject which is apparently resting on a dead center of perfectness. At the present day it seems fashionable to suppose that certain views are so firmly established that no research into their foundations is worth the labor expended on it . . . it was supposed for many years that the composition of the atmosphere was definitely settled—and then the discoveries of Rayleigh and Ramsay showed how little was known of even this common mixture. With this object lesson before them, it is to be hoped that more organic chemists will find time to investigate some of the problems which are passed over by the bulk of workers who seem to place a label in the same category as an explanation."

The x-ray examination of optically active organic compounds is a field which is thus far practically untouched. No one has yet used the powerful rotating crystal method in a study of this type. W. T. Astbury[3] has made a study of d-tartaric acid, utilizing axial ratios and angles determined by optical methods, and measuring interplanar spacings by means of the Bragg spectrometer method. He finds that his results confirm the theory of van't Hoff and Le Bel, and that it is not possible to distinguish between the d- and l-forms of an optically active substance by means of x-ray diffraction methods.

Reis and Schneider[4] have recently presented further x-ray data for tartaric and mesotartaric acids.

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[1] From a part of the thesis submitted by G. R. Yohe to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Stewart, "Recent Advances in Organic Chemistry," 1927, Vol. I, p. 18.

[3] Astbury, *Proc. Roy. Soc. London*, **102A**, *506* (1923).

[4] Reis and Schneider, Z. *Krist.*, 69, 62, 49 (1928).

There are two hundred and thirty space groups according to which crystals may be built. While most of these space groups can be built up of molecules which possess symmetry within their structure, there are a few which will admit of no molecular symmetry. If, in crystallizing, an optically active compound builds its crystalline form according to one of these space groups which will admit of no symmetry of the molecule this may be taken as direct evidence that its molecules are asymmetric. For this study a representative amino acid, phenylaminoacetic acid, was chosen in spite of the fact that no crystallographic or optical data are available in Groth's tables or elsewhere for the active or racemic forms of this compound. One of the chief purposes of the investigation was to show that a unique structural analysis can be made by means of x-ray diffraction results alone and without adopting the invariable practice of depending upon previous crystallographic information. The rotating crystal diffraction method has been made to combine goniometric orientation of crystals and the production of the fruitful layer-line patterns for rotation around three principal axes.

Experimental

A. The Phenylaminoacetic Acid Used.—Phenylaminoacetic acid was being resolved in connection with another investigation, and the d-, *l*- and dl-forms at hand were subjected to this x-ray examination.

The crude phenylaminoacetic acid was prepared at the University of Illinois by the following reactions[5]

$$C_6H_5CHO + NaCN + NH_4Cl \longrightarrow C_6H_5CHNH_2CN + NaCl + H_2O$$
$$C_6H_5CHNH_2CN + HCl + 2H_2O \longrightarrow C_6H_5CHNH_2COOH + NH_4Cl$$

It was found that the racemic amino acid could be recrystallized from hot dilute pyridine (2 volumes of water to 1 of pyridine), and that by very slow cooling of the solution well-formed crystals could be obtained. These were very small, however, the largest being about one mm. long and less than one mm. in thickness; m. p. 250–252°, uncorr.

The levorotatory form was obtained by following the procedure of Ingersoll and Adams,[6] which is essentially that of Betti and Mayer,[7] of fractional crystallization of the d-camphorsulfonate, the *l*-phenylaminoacetic acid d-camphorsulfonate being less soluble. Since the d-camphorsulfonate hydrolyzes readily in hot water, it was found best to use an excess of d-camphorsulfonic acid in this resolution. The separation of the forms was carried out as follows: 110 g. of dl-phenylaminoacetic acid, 206 g. of d-camphorsulfonic acid and 500 cc. of water were heated together, giving a clear solution which on cooling deposited crystals of the *l*-phenylaminoacetic acid d-camphorsulfonate. These were recrystallized from hot water using about 10% excess of d-camphorsulfonic acid to prevent hydrolysis and about 2 g. of Norite to decolorize the solution. The *l*-phenylaminoacetic acid was precipitated from a cold, saturated, aqueous solution of the *d*-

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[5] Adams and Marvel, "Organic Chemical Reagents," 1922, Vol. IV, p. 24.

[6] Ingersoll and Adams, THIS JOURNAL, 44, 2930 (1922).

[7] Betti and Mayer, Ber., 41, 2071 (1908).

camphorsulfonate by adding dilute ammonium hydroxide until the solution was faintly alkaline. The crystals, after washing with water and drying, gave a rotation $[\alpha]_D^{20}$ $-152°$ in 0.133 N hydrochloric acid; $[\alpha]_D^{20}$ $-162.8°$ in 10% hydrochloric acid; $[\alpha]_D^{20}$ $-111°$ in water, this last value checking that of $-111.02°$ given by Betti and Mayer.[7] It was found that on slow evaporation of a saturated aqueous solution of the *l*-phenylaminoacetic acid, long needle-like crystals formed. One of the most perfect of these was used in the rotating crystal studies; m. p., subl. 245–248°, uncorr.; $[\alpha]_D^{20}$ (in 0.140 N hydrochloric acid) $-149°$. It may be noted here that the rotations observed varied widely with the concentration of the hydrochloric acid used as a solvent. No consistent melting point was obtained, which is in harmony with the results previously published. For example, St. Minovici[8] reports m. p. 227° (subl.); Fischer and Weichhold[9] report m. p. 305–310°; Betti and Mayer[7] report m. p. above 305°.

The d-phenylaminoacetic acid was obtained by extraction of the partially resolved (80% d-, 20% *dl*-phenylaminoacetic acid) acid precipitated from the mother liquor of the d-camphorsulfonate crystallization with ammonium hydroxide. The active form of phenylaminoacetic acid is more readily soluble in hydrochloric acid than the racemic, and is thus extracted from the racemic.[10] The d-phenylaminoacetic acid was precipitated by adding dilute ammonium hydroxide. The mother liquor from this precipitation, on standing for several days, yielded needle crystals, one of the most perfect of which was used in the x-ray work; m. p. 242–244°, uncorr.; $[\alpha]_D^{20}$ (in 0.105 N hydrochloric acid) $+147°$.

B. The **X-Ray** Equipment.—The x-ray tube used was of the Hadding–Siegbahn type equipped with a copper anticathode. It was operated at about 40 kilovolts and a current of about 12 milliamperes, the high potential being supplied by a Wappler special transformer, rectified by a Kenex rectifier. The radiation was not filtered, the K_α radiation of copper predominating to such an extent that filtration was found unnecessary.

A Müller Universal Spectrograph was used. This was equipped with a cylindrical camera of 5-cm. radius, and a goniometer head which greatly facilitated the accurate orientation of the crystal, as well as making it possible to measure the angles between the crystallographic axes by measuring the displacement necessary to bring another crystallographic axis parallel to the axis of rotation.

The time of exposure depended upon the focus of the cathode rays within the x-ray tube. A good focus giving a very intense beam of x-rays made possible the taking of good pictures in one to two hours' exposure, but for poorer focus and hence a less intense x-ray beam exposures of ten hours were necessary.

C. The Technique of Taking the Photographs.—The levorotatory form was studied first. The needle-like crystal was mounted on the goniometer mounting with a small drop of collodion so that the long axis of the crystal was perpendicular to the axis of rotation. The resulting photograph showed the crystal to be improperly aligned. The angle between

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[8] St. Minovici, Bull. *Soc. Chim.* **Romania, 2,** 8 (1910).

[9] Fischer and Weichhold, Ber. 41, 1286 (1908).

[10] Unpublished work from this Laboratory.

the two lines of interferences that cross at the position of the central beam was measured, and the crystal displaced half this angle, still keeping the long axis of the crystal perpendicular to the axis of rotation. By this means it was possible to bring the crystal into alignment so that one of the major crystallographic axes was parallel to the axis of rotation. The resulting layer line diagram is reproduced in Fig. 1. The crystal was then displaced 90°, still keeping the long axis of the crystal perpendicular to the axis of rotation. Another typical layer line diagram was thus obtained showing that another major crystallographic axis was now parallel to the axis of rotation, and that the angle between the two axes was 90°. The crystal was then displaced another 90°, this time bringing the long axis of the crystal parallel to the axis of rotation. Again a typical layer line diagram was produced showing that the third crystallographic axis was now parallel to the axis of rotation, and that the angle between this third axis and the plane of the first two must be 90°.

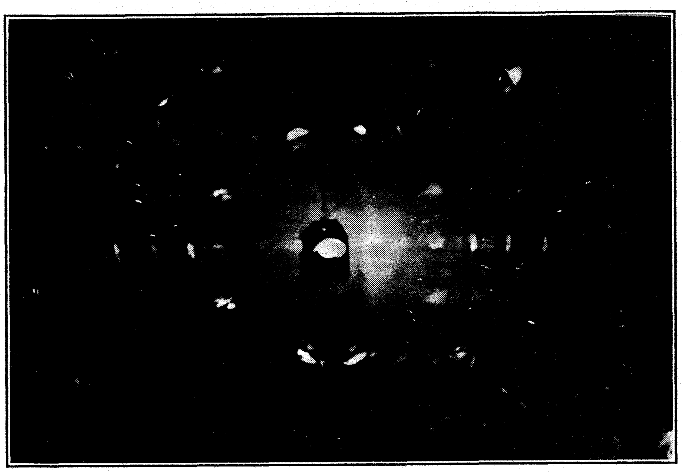

Fig. 1.

In this way the crystal was proven orthorhombic, independently of any optical data, since $\alpha = \beta = \gamma = 90°$. The layer lines of the rotation photographs make possible direct calculation of the "identity periods," or dimensions of the unit cell, and consequently the axial ratio in a manner which is verly clearly explained by Sir William Bragg.[11]

It is of interest to note the size of the crystals used in making these photographs, and others made of the dextrorotatory and racemic modifications. The dimensions of the crystal of 1-phenylaminoacetic acid were 4 mm. X 1 mm. X 0.1 mm.; those of the crystal of the d- form used were 4 mm. X

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[11] Bragg, "An Introduction to Crystal Analysis," D. Van Nostrand Co., New York, 1929, p. 41.

0.3 mm. × 0.2 mm.; and those of the crystal of the racemic form were about 2 mm. × 1 mm. X 0.5 mm. Thus it may be seen that very small crystals can be used in work of this type; in fact it is advantageous to use small crystals since the resulting diffraction spots are sharper and can be measured more accurately. Furthermore, a small crystal is more apt to be free from imperfections.

D. Data for *l*-Phenylaminoacetic Acid.—In calculating the identity periods from the layer line photographs, use was made of the equation

$$I = \frac{n\lambda}{\sin \mu}$$

where **I** is the identity period, *n* the number of the layer line (i.e., 1st, 2nd, 3rd, ...), λ the wave length of the radiation used (λ Cu K_α = 1.54 Å.), and $\mu = \tan^{-1} e/a$, e being the distance measured on the film from the equator line to the nth layer line, a being 50 mm., the distance from the axis of rotation to the film. The following tables give the results obtained in calculating these identity periods.

TABLE I

DATA FROM FILM REPRODUCED IN FIG. 1 FOR IDENTITY PERIOD ALONG *c* AXIS

Goniometer scale readings: 13° 50′, 26° 20′

e, mm.	tan μ	sin μ	*n*	*I*, Å.
8	0.1600	0.1579	1	9.74
17	.3400	.3220	2	9.55
27	.5400	.4751	3	9.70
			Average	9.66

TABLE II

DATA FOR IDENTITY PERIOD ALONG *a* AXIS

Goniometer scale readings: 13° 50′, 116° 20′

e, mm	tan μ	sin μ	*n*	I. A.
5.2	0.1040	0.1034	1	14.9
10.5	.2100	.2056	2	15.0
15.8	.3160	.3013	3	15.3
21 8	.4360	.3996	4	15.4
			Average	15.2

TABLE III

DATA FOR IDENTITY PERIOD ALONG b AXIS

Goniometer scale readings: 103° 50′, 54° 00′

e, mm.	tan μ	sin μ	*n*	I, Å.
16	0.3200	0.3049	1	5.05

Though no more layer lines were obtained, this value of **I** checks exactly with values taken from a photograph using a flat film and stationary crystal, in which interferences corresponding to two layer lines were obtained, both values being 5.05 Å.

Thus the dimensions of the unit cell are calculated directly to be a = 15.20, b = 5.05 and *c* = 9.66 Å. (axial ratio 3.01 : 1 : 1.91) and, since the unit cell is orthorhombic, the volume of this cell is 15.20 × 5.05 × 9.66 Å.^{3} = 742 Å.^{3}

The density of the crystals was obtained by suspending them in a liquid of known density. The liquid used was petroleum ether. Although *l*-phenylaminoacetic acid is insoluble in petroleum ether within the limits of error of this determination, the precaution was taken to allow the petroleum ether to stand in contact with the I-phenylaminoacetic acid for several hours before the determination was started. The density so obtained is 1.30.

Then N, the number of molecules in the unit cell, is obtained from

$$N = \frac{(\text{volume of unit cell})\ \text{X}\ (\text{density})}{\dfrac{(\text{mass of H atom})}{(\text{molecular wt.})} \times (\text{Avogadro's number})}$$

$$N = \frac{5.05 \times 9.66 \times 15.2 \times 10^{-21} \times 1.30}{(151/1.008) \times 1.663 \times 10^{-24}} = 3.88$$

This is very nearly four, so that N, the number of molecules in the unit cell, is taken as four.

Thus it was shown that *l*-phenylaminoacetic acid is orthorhombic, and contains four molecules per unit cell. These considerations alone would narrow down the possible space groups to the following:[12] C_{2v}^1, C_{2v}^2, C_{2v}^3, C_{2v}^4, C_{2v}^5, C_{2v}^6, C_{2v}^7, C_{2v}^8, C_{2v}^9, C_{2v}^{10}, Q^1, Q^2, Q^3, Q^4, all of which are based on Rravais lattice Γ_0. In the C_{2v} space groups the a and *b* axes are interchangeable. Of these space groups, C_{2v}^1 and Q^1 are at once eliminated as they call for no abnormal spacings; in these results (see Tables IV, V and VI) it is seen that the 9.66 spacing appears only as the identity period

TABLE IV

Interferences on Equator Line of Fig. 1, *l*-Phenylaminoacetic Acid. Crystal Rotated around the c Axis (= 9.66 Å.)

In Col. 1 the following abbreviations are used: vs = very strong, s = strong, m = medium, f = faint, vf = very faint. In Col. 2, the arc measured is the distance on the film from a spot to the corresponding spot on the other side of the central beam. Θ is the angle between the central beam and the diffracted beam.

Intensity	Arc, mm.	Θ, radians	Θ, degrees	Θ/2	Sin Θ/2	*d*, Å.
vs	10.0	0.100	5° 44′	2° 52′	0.0500	15.4
f	20.3	.203	11° 40′	5° 50′	.1016	7.58
Broadanddiffuse	30.0	.300	17° 10′	8° 35′	.1493	5.16
	314	.314	18° 00′	9° 00′	.1564	4.92
	325	.325	18° 40′	9° 20′	.1623	4.75
f	36.9	.369	21° 10′	10° 35′	.1837	4.19
vs	40.8	.408	23° 25′	11° 43′	.2031	3.79
vf	46.0	.460	26° 20′	13° 10′	,2278	3.38
	46.0	Using Cu Kg wave length				3.05
s	51.2	.512	29° 20′	14° 40′	.2532	3.04
vf	55.9	.559	32° 00′	16° 00′	.2756	2.80
	55.9	Using Cu Kg wave length				2.52
vs	62.0	.620	35° 30′	17° 45′	.3049	2.52
vf	832	.832	47° 40′	23° 50′	.4041	1.91

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[12] Astbury and Yardley, "Tabulated Data for the Examination of the 230 Space Groups by Homogeneous X-rays," **Phil.** Trans. Roy. *Soc.* London, 2248,221 (1926).

TABLE V

INTERFERENCES ON EQUATOR LINE POR CRYSTAL ROTATED AROUND 15 2 AXIS (a OR *b)*

Intensity	Arc, mm	Θ, radians	Θ, degrees	9/2	Sin 8/2	*d*, Å
s	332	0332	19° 00′	9° 30′	01651	466

TABLE: VI

INTERFERENCES ON EQUATOR LINE POR CRYSTAL ROTATED AROUND 5 05 AXIS *(a* OR *b)*

Intensity	Arc, mm.	Θ, radians	Θ, degrees	Θ/2	Sin Θ/2	d, Å
vs	102	0102	5° 50′	2° 55′	00509	15.1
f	20 3	203	11" 40'	5" 50'	.1016	7 58
vvf	25 6	256	14° 40'	7° 20'	.1276	6 04
s, broad	33 0	.330	18° 54'	9° 27'	1642	4 68
vf	39 5	395	22° 40'	11' 20'	1965	3 92
f	36 8	368	21° 4'	10° 32'	.1828	4 22
	36 8	Using Cu Kg wave length				3 80
vs	41 0	410	23° 30'	11° 45'	.2036	3 79
vf	43 3	433	24° 50'	12° 25'	2150	3 58
vf	46 2	462	26° 30'	13° 15'	2292	3.36
	46 2	Using Cu K_β wave length				3 03
vs	51 0	510	29° 10'	14° 35'	2518	3 06
f	55 6	556	31° 50'	15° 55'	2742	2 81
	55 6	Using Cu K_β wave length				2 53
s	61 8	618	33° 25'	17° 47'	3054	2 52
vf	64 0	640	36° 40′	18° 20'	3145	2 45
vvf	67 4	674	38° 36'	19° 18'	3305	2 33
	67 4	Using Cu K_β wave length				2 10
vf	74 3	743	42° 34'	21° 17'	3630	2 12
vf	83 9	839	48° 4'	24° 2'	4073	1 89
f	90 0	900	51° 34'	25° 47'	4350	1 77

(Table I), not as true first order reflection, and again halved, as 4.84 (Table IX). The same is true also of the 5.05 spacing. Q^3 and Q^4 are eliminated readily since they call for the halving of both {1 0 0) and {0 1 0}, while the 15.2 spacing appears very strongly in these results. Space group C_{2v}^2 calls for halving of {0 k I] if I is odd; this condition is fulfilled (Table VIII). C_{2v}^3 requires halving of {h 0 I} if I is odd; this is not true, and C_{2v}^3 is eliminated (Table VII). In C_{2v}^4 {*h* 0 *l*} is halved if h is odd; that this is true may be seen in Table VII. C_{2v}^5 calls for halving of {h0 I} if h is odd, and halving of {0 k *l*} if *l* is odd. Tables VII and VIII show both of these conditions to be fulfilled, and since C_{2v}^2 calls for only the latter of these two, and C_{2v}^4 for only the former, these two are eliminated. C_{2v}^6 and C_{2v}^7 require that {*h* 0 *l*} be halved if h + I is odd; Table VII shows that this is not the case, thus eliminating these two. In C_{2v}^8 {0 k *l*} must be halved if k is odd; Table VIII shows that this is not the case. C_{2v}^9 and C_{2v}^{10} call for halving of {0 k I] if k + *l* is odd; that this is not the case is readily seen from Table VIII. This leaves only space groups C_{2v}^5 and Q^2. Q^2 calls for only one abnormal spacing, the halving of {0 0 1}.

That other abnormal spacings occur can be seen from Tables VII and VIII; these two tables also show remarkable agreement with the conditions required for space group C_{2v}^5. The conclusion is, therefore, that *l*-phenylaminoacetic acid belongs to space group C_{2v}^5, which by its purely geometric derivation demands four asymmetric molecules per unit cell.

TABLE VII

SPACE GROUP ASSIGNMENT

One of the conditions for space group C_{2v}^5 is that $(h0l)$ must be halved if h is odd. This condition also applies to space group C_{5v}^9. In this table Col. 3 − means that the spacing indicated should not appear, + means that it should. The observed values are taken from the photograph for which the crystal was rotated about the 5.05 axis; calculated spacings based on a = 15.2, b = 5.05.

1 *h* 0 1	2 d	3	4 Observed spacing	5 Other possible planes
100	15 2	−	15 1	
200	7 60	+	7 58	
300	5 06	−		
400	3 80	+	3 79	
500	3 04	−	3.06	402, 203
600	2 53	+	2 52	
700	2 17	−	2 12?	
800	1 90	+	1 89	205, 801, 005
001	9 66	+		
002	4 83	+	[a]	
003	3 22	+		
004	2.42	+	2 44	
005	1 93	+	1 89	205, 801, 800
101	8.15	−		
102	4.61	−	4 68	
103	3 16	−		
104	2 39	−		
105	1 92	−	1 89	205,801,800,005
201	5 94	+	6 04	
202	4 07	+	3 92[b]	
203	2 97	+	3.06	402
204	2 30	+	2 33[c]	
205	1 87	+	1 89	801,800,005
301	4 49	−		
302	3 50	−	3 58	401
303	2 71	−		
304	2.18	−	2 12	404?
305	1.80	−		
401	3.56	+	3.58	
402	2 99	+	3 06	203
403	2 46	+	2 45	601
404	2.04	+	2 12	
405	1.72	+		
501	2 90	−	3 06	203, 402
502	2.56	−	2 52	600
503	2.21	−		
504	1 89	−	1 89	205, 801, 800, 005
601	2 45	+	2 45	403
602	2 25	+		
603	1.98	+		
604	1.75	+	1.77	802
701	2 12	−	2.12	404?
702	1.99	−		
703	1.81	−		
801	1 87	+	1 89	205, 800, 005
802	1.78	+	1.77	604

[a] This is in a region where apparently several interferences lie close together, giving a broad diffuse spot. Using a smaller crystal of the d-form, sharper spots were obtained; one was found corresponding to d = 4.84 A. [b] Very faint. [c] Possibly Cu K_β line from spacing 2.10 Å.

Wyckoff[13] gives the following as the coordinates of the four equivalent points in space group C_{2v}^5: (x, y, z), $(\bar{x}, \bar{y}, z + 1/2)$, $(x + 1/2, \bar{y}, z)$, $(1/2 - x, y, z + 1/2)$. A drawing of the unit cell is shown in Fig. 2. Since any point on the lattice may be chosen as the origin, a different origin has been selected for each of the four points in such a way that all four points fall in

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[13] Wyckoff, "Analytical Expression of the Results of the Theory of Space Groups," Carnegie Institution, Washington, 1922, p. 22.

TABLE VIII

SPACE GROUP ASSIGNMENT

A comparison of C_{2v}^5 and C_{2v}^9, based on whether {0k l) is halved if l is odd or if (k + l) is odd. As in Table VII − indicates that the interference should not appear, + indicates that it should appear. Measurements in Col. 5 were taken from the equator of the film for the crystal rotated about the 5.05 axis; calculated spacings based on a = 5.05. b = 15.2.

1 0 *k l*	2 *d*	3 C_{2v}^5	4 C_{2v}^9	5 Obs. spacing	6 Other possible planes
001	9.66	−	−		
010	15.2	+	−	15.1	
002	4.83	+	+	[a]	
003	3.22	−	−		
004	2.42	+	+	2.45	
005	1.93	−	−		
020	7.60	+	+	7.58	
030	5.06	+	−		
040	3.80	+	+	3.79	
050	3.04	+	−	3.06	042
060	2.53	+	+	2.52	052
070	2.17	+	−	2.12	034
080	1.90	+	+	1.89	054
011	8.15	−	+		
012	4.61	+	−	4.68	
013	3.16	−	+		
014	2.39	+	−	2.33[b]	024
015	1.92	−	+		
021	5.94	−	−	6.04	
022	4.07	+	+		
023	2.97	−	−	3.06	042
024	2.30	+	+	2.33[b]	014
025	1.87	−	−	1.89	054,080
031	4.49	−	+		
032	3.50	+	−	3.58	
033	2.71	−	+		
034	2.18	+	−	2.12	070
035	1.80	−	+		
041	3.56	−	−	3.58	032
042	2.99	+	+	3.06	050
043	2.46	−	−	2.45	004
044	2.04	+	+		
045	1.72	−	−		
051	2.90	−	+	3.06	042, 050
052	2.56	+	−	2.52	060
053	2.21	−	+		
054	1.89	+	−	1.89	080
061	2.45	−	−	2.45	004
062	2.25	+	+		
063	1.98	−	−		
064	1.75	+	+	1.77	082
071	2.12	−	+	2.12	034,070
072	1.99	+	−		
073	1.81	−	+		
081	1.87	−	−	1.89	054,080
082	1.78	+	+	1.77	064

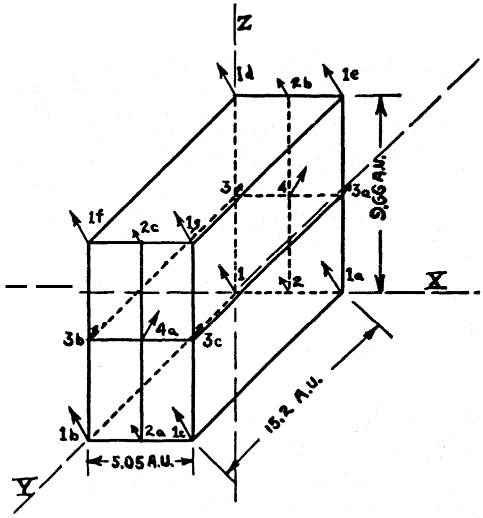
[a] See note a under Table VII. [b] See note c under Table VII.

the same unit parallelopiped. The other points that have the same relation to the lattice as these four are then placed. There are thus eight molecules at the eight corners of the cell. Since each of these is shared by eight unit parallelopiped~, one-eighth of these, or one, belongs to one unit cell. There are eight others that lie on edges of the parallelopiped. Each of these is shared by four unit parallelopiped~, whence one-fourth, or two, belong to the one unit cell. There are two more that lie in faces of the parallelopiped; since each of these is shared by two cells, one-half of these, or one, belongs to the one cell. Thus the total is four molecules per unit cell. It readily can be seen from the drawing that two of the spacings corresponding to the unit cell dimensions will be halved, while the third will not. As was observed above, the 9.66 and 5.05 Å. spacings did not appear except on the layer line diagrams, while the 15.2 Å. spacing was not halved. It may also be seen that the (0 1 0) planes are densely populated with molecules; this explains the high intensity of the reflections from these planes.

It is evident that the *c* axis (identity period 9.66 Å.) differs from the *a* and *b* axes in that it coincides with the dyad screw axis of symmetry.[12]

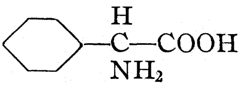
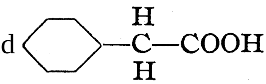
In explanation of Fig. 2, Arrow 1 is considered pointing behind the ZX plane and to the left of the YZ plane. Arrows 1 a, b, c, d, e, f and g are parallel to 1. Arrow 2 points in front of the ZX plane and to the left of a plane parallel to YZ. Arrows 2 a, b and c are parallel to 2. Arrow 3 points in front of the ZX plane and to the right of the YZ plane. Arrows 3 a, b and c are parallel to 3. Arrow 4 points behind the ZX plane and to the right of a plane parallel to YZ. 4a is parallel to 4. By a rotation of 180° and a translation of $c/2$, 1 will coincide with 3, 2 with 4, etc.

No attempt is made here to determine the orientation of the molecules within the unit cell other than the molecular asymmetry demanded by the space group, and the relative positions of the molecules as shown in the diagrams. To determine the relative positions of the atoms within any one molecule, and to determine just how these atoms are situated with respect to the axes requires careful measurement of the intensities of various reflections; even then many assumptions must be made. In this investigation it was considered that the intensity data were not sufficient and that the assumptions involved were not justifiable for the calculating of molecular sizes, shapes and orientations within the unit cell. Obviously the molecules must lie with their greatest length in the general direction of the *a* axis (15.2 Å.).



The four equivalent positions are shown at 1, 2, 3 and 4.

Fig. 2.—Diagram of the unit cell of active phenylaminoacetic acid, $C_6H_5CHNH_2COOH$.

It is of interest to compare the structure of active phenylaminoacetic acid  $C_6H_5-\overset{H}{\underset{NH_2}{C}}-COOH$ (I) with that of phenylacetic acid  $C_6H_5-\overset{H}{\underset{H}{C}}-COOH$ (11), recently studied by Patterson.[14]

	I	II
Melting point, ° C.	248 or higher	76.5
System	Orthorhombic	Monoclinic

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[14] Patterson, *Phil.* Mag., 3, 1252 (1927).

	I	II
Space group	C_{2v}^5	C_{2h}^5 (b)
Molecules per unit cell	4	4
a	15 2	14.2
b	5.05	4 90
c	9 66	10.1
β	90°	101°
***h* k *l* halvings**	*h* 0 *l*, **hodd**; 0 *k* *l*, *l* odd	0 1 0; *h* 0 *l*, *l* odd
Molecular symmetry	**None**	**Center**

The dimensions of the unit cells are remarkably similar and the comparison further verifies the correctness of the structure assigned. The presence of the basic amino and acid carboxyl groups in the same molecule affects profoundly the forces holding the molecule in the unit cell, as clearly shown by the inordinately high melting point. This is a further complication in interpretation of intensity data.

It is very important to note that the space group C_{2v}^5 admits of no possible molecular symmetry. Thus the classical theories of van't Hoff and Le Bel are confirmed, for here an examination has been made of an optically active substance, and the space group of the crystal requires that the molecule be asymmetric.

E. The Structure of d-Phenylaminoacetic Acid.—A rotation diagram of a crystal of this enantiomorph gave identically the same results as for the 1-acid. For the rotation around the b (5.05 Å.) axis the 15.2 Å. spacing shows up strongly. It is interesting to note here that the 9.66 Å. spacing appears halved, as spacing 4.84 Å., while for the levo form there was no clearly defined interference. This is due to the fact that the crystal of dextro form used was smaller, and therefore the interferences were more distinct than on the film from the 1-form, where the use of a larger crystal gave a more diffuse spot at the corresponding position. Powder photographs made with the General Electric X-Ray Diffraction apparatus, using the K_α radiation of molybdenum present further proof of the identity of the two active forms of phenylaminoacetic acid. It is thus quite clear

TABLE IX

MEASUREMENTS FOR *d*-PHENYLAMINOACETIC ACID

$a = 50$, $e = 16$, **therefore I = 5.05 Å. (see Table III). Interferences on Equator Line.**

Intensity	Arc, mm	Θ, radians	Θ, *degrees*	Θ/2	Sin Θ/2	*d*, Å.
s	10 2	0.102	5° 50'	2° 55'	0.0509	15.1
f	32.0	.320	18° 20'	9° 10'	.1593	4.84
ms	33.0	.330	18° 54'	9° 27'	.1642	4.68
s	34.7	.347	19° 52'	9" 56'	,1725	4.46
f	35.8	.358	20° 30'	10" 15'	.1779	4 33
f	39.2	.392	22° 30'	11° 15'	.1951	3.94
vf	44 0	.440	25" 10'	12° 35'	.2179	3 54
f	57.0	.570	32° 40'	16" 20'	.2812	2.74
vf	68 1	.681	39° 00'	19° 30'	.3338	2.31

that the structure of d-phenylaminoacetic acid is the same as that of the l-form, and that these results show that X-ray diffraction methods offer no means of distinguishing between the two.

F. Study of the Racemic Modification.—A complete analysis of the crystalline structure of the racemic modification of phenylaminoacetic acid will be presented in another paper. However, ample proof is at hand that it differs from the active forms. In the powder spectra it can be readily seen that there is no correspondence of diffraction lines between active and racemic forms. A rotating crystal photograph of the racemic form was made using the same apparatus as described above. The identity period calculated from this photograph is 4.26 Å., differing widely from any observed in the case of the active form. This evidence is sufficient to prove that the racemic form has a different crystalline structure than the active forms.

Summary

1. An x-ray examination by the rotation and powder diffraction methods has been made of the *d*-, *l*- and racemic forms of phenylaminoacetic acid. The power of the rotation method is shown by the fact that a straightforward crystal structure analysis was possible although no crystallographic or optical data were available.

2. The d- and *l*- forms are shown to crystallize in the orthorhombic system, upon Bravais lattice Γ_0, space group C_{2v}^5. The unit cell containing four molecules has the dimensions $a = 15.2$, $b = 5.05$, $c = 9.66$ Å.

3. The fact that space group C_{2v}^5 admits of no molecular symmetry confirms the classical theories of van't Hoff and Le Bel connecting molecular asymmetry with optical activity.

4. It has not been found possible to distinguish between the d- and *l*-forms by means of x-ray diffraction methods.

5. The crystal form of the racemic modification differs from that of the optically active forms.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

SOME ORGANIC ACIDS OF SUGAR CANE MOLASSES

BY E. K. NELSON

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In continuation of the work in this Laboratory on the non-volatile acids of fruits and plant products, an investigation was made of the acids of sugar cane molasses.[1] While considerable work has been done on this subject, it appeared to be worth while to determine the acids of molasses by the ester distillation method.

The organic acids of cane molasses comprise the acids naturally occurring in cane juice, chiefly aconitic acid, and the acids formed during the process of manufacture, such as formic, acetic and lactic acids. Of the amino acids formed from the hydrolysis of proteins, aspartic and glutamic acids have been found in molasses. Dark colored uncrystallizable acids are also present, but none of these is considered in the present paper.

The presence of aconitic acid in cane juice was first noted by Arno Behr,[2] who separated it in the form of an acid ammonium salt.

Malaguti[3] records that although oxygen is without influence on neutral sugar solutions, formic acid is formed in the presence of weak acids. He concluded that the acid caused partial inversion and that the formic acid resulted from the action of oxygen on invert sugar. As early as 1851, formic and acetic acids were mentioned by Michaelis[4] as being present in beet molasses, and this has been confirmed by later investigations.

It has been shown by numerous investigators, among whom may be mentioned Niedschlag,[5] Isaac[6] and Tollens,[7] that acetic and lactic acids are formed by the action of alkalies on sucrose, and Tollens states that the lime treatment of beet juice probably produces most of the lactic acid found in the products of sugar manufacture, and that this acid may amount to 0.5% of the molasses.

More recently the acids in sugar cane juice have been investigated by Yoder,[8] who found aconitic acid and a small quantity of malic acid. From 6 liters of juice Yoder isolated 3 g. of aconitic acid and 0.046 g. of malic acid. He reported the absence of tartaric, succinic and citric acids.

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[1] Acknowledgment is made to Dr. C. A. Browne, Assistant Chief of the Bureau of Chemistry and Soils, for suggesting this problem and for his helpful and sustained interest throughout the progress of the work.

[2] Behr, *Ber.*, 10, 351 (1877).

[3] Malaguti, *Ann. Chemie*, [2] 59, 412 (1835).

[4] Michaelis, *Z. Verh. Rubenzucker-ind.*, 1, 114 (1851).

[5] Niedschlag, *Die Deutsche Zucker-ind.*, 12, 159 (1887).

[6] Isaac, *Chem. News*, **66**, 39 (1892).

[7] Tollens, *Z. Verh. deutsche Zucker-ind.*, (O. S.) 39, 322 (1889); *Ann.*, 255, 228 (1889).

[8] Yoder, *J. Ind. Eng. Chem.*, 3, 640 (1911).

The material used in the investigation reported in this paper was a sample of molasses from the Central Fajardo, Porto Rico.[9] The analysis accompanying the sample was as follows: Brix, 83.90; dry substance, 83.86; apparent purity, 31.00; true purity, 36.54; glucose, 28.86; sucrose, 30.64; ash, 7.52; dye value,[10] 3373.

The alkalinity of the ash was equivalent to 57.1 cc. of normal hydrochloric acid per 100 g. of sample and the free acid corresponded to 26.0 cc. of normal hydrochloric acid per 100 g.

The volatile acids consisted of a mixture of formic and acetic acids, 0.097 g. of formic and 0.2 g. of acetic acid being recovered per 100 g. of molasses.

The predominating non-volatile acid was aconitic acid (0.8%). Small quantities of malic, citric and lactic acids were found.

Experimental

Volatile Acids.—Volatile acids were distilled from three kilos of molasses to which sufficient hydrochloric acid had been added to liberate the combined acids. The distillate was neutralized with standard barium hydroxide solution and evaporated to dryness. The dried barium salts were weighed and from the weight, taken in conjunction with the quantity of barium necessary to neutralize the distillate, the proportion of barium formate and barium acetate was calculated.

The distillate required 657 cc. of 0.25 *N* barium hydroxide to neutralize it, and the barium salts weighed 20.089 g. From these data the weight of the barium formate was calculated to be 7.195 g. and that of the barium acetate, 12.894 g.

Non-Volatile Acids.—The non-volatile acids were precipitated as lead salts from two kilos of molasses. The acids recovered from the lead salts were dissolved in water and extracted four times with ether. The ether removed 4.06 g. of a crystalline acid melting at 185 to 186° and giving no depression in melting point on admixture with aconitic acid. The aqueous solution was then evaporated to dryness, esterified in the usual manner and the esters, 7.8 g., were fractionated at 10 mm. Less than 1 cc. distilled under 150°. This distillate afforded a hydrazide crystallizing like malic hydrazide, melting at 178 to 179° and showing no depression in melting point when mixed with malic hydrazide.

Fraction **2,** when redistilled, boiled at 160° and weighed 4.5 g. As the hydrazide of aconitic acid is very hygroscopic and not easily identified, this fraction was saponified, acidified and extracted with ether, yielding pure aconitic acid. Four and one-half grams of ethyl aconitate correspond to three grams of aconitic acid.

The third fraction, boiling above 160°, measured 0.5 ec. When this fraction was treated with hydrazine hydrate, a hydrazide separated which had the appearance of citric hydrazide. It melted at 100 to 103°. Optical crystallographic examination[11] proved its identity as citric hydrazide.

In order to avoid losses by esterification, a direct, continuous ether extraction was made on the acids recovered by precipitation of three kilos of molasses with lead acetate.

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[9] The Carbohydrate Division of this Bureau furnished material for this investigation with the analysis of the sample.

[10] Badollet and Paine, *Int.* Sugar ***Journal,*** 28, **23,** 97, 137 (1926).

[11] This examination was made by G. L. Keenan of the Food, Drug and Insecticide Administration.

The concentrated solution of the acids was extracted in a Bacon-Dunbar "perforation" outfit until only negligible quantities of extractive were removed by the ether. In this manner 23.9 g. of aconitic acid was obtained, or 7.97 g. per kilo.

The acid solution remaining after the extraction by ether was neutralized with calcium carbonate, the excess being removed by filtration. The solution, on boiling, deposited a considerable precipitate. Filtered and dried, this weighed 1.76 g. The acid isolated from this calcium salt melted at 142 to 144° and gave no depression when mixed with citric acid. Optical crystallographic examination confirmed its identity as citric acid.

A special examination of Dominican molasses was made for lactic acid. Four hundred grams of molasses was acidified, diluted with 200 cc. of water and extracted for twenty-four hours with a rapid stream of ether in a perforation outiit. The ether-soluble acids were neutralized with barium hydroxide, diluted to 100 cc. and then 200 cc. of alcohol was added. After this solution had stood overnight, the undissolved barium salts were filtered off. The filtrate was freed from barium with the required quantity of sulfuric acid, the filtrate from barium sulfate was boiled with an excess of zinc carbonate and filtered. The filtrate was concentrated to 5 cc., 15 cc. of alcohol was added and the crystalline precipitate was filtered, dried and weighed. It weighed 0.315 g., corresponding to 0.19 g. of lactic acid, or 0.05% of the molasses. Optical crystallographic examination, oxidation to acetaldehyde and the hydroxy acid test with ferric chloride established its identity as zinc lactate.

The acids recovered from the insoluble barium salt were subjected to fractional crystallization. All fractions were aconitic acid. No succinic acid or tricarballylic acid could be separated from any of the fractions or identified by optical crystallographic examinations.

Summary

The acids of molasses were found to be formic acid, about 0.1%; acetic acid, 0.2%; aconitic acid, 0.8%; lactic acid, 0.05% and small quantities of malic and citric acids. By establishing the presence of formic, acetic, aconitic, malic and lactic acids in sugar cane molasses, the results of previous investigators were confirmed. Citric acid has not previously been reported as a constituent of sugar cane molasses.

WASHINGTON, D. C.

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

III. THE CHEMICAL EFFECTS OF SEMI-CORONA DISCHARGE IN GASEOUS HYDROCARBONS[1]

BY S. C. LIND[2] AND GEORGE GLOCKLER[3]

RECEIVED MAY 10, 1929 PUBLISHED SEPTEMBER 5, 1929

In two previous papers[4] the authors showed that when ethane is subjected to electrical discharge of various types, condensation to liquid by the elimination of hydrogen and methane always takes place. The identity of the gaseous products and of their amounts relative to those found when alpha particles act on hydrocarbons[5] led to the conclusion that the reactions are entirely similar in being due to ionization. Hence the same kind of mechanism is operative in both cases. Especially is that true of the less intense types of discharge such as in the ozonizer or Siemens tube. In corona and semi-corona discharge, while the gaseous and liquid products remain the same, formation of solid on the walls also occurs. In the semi-corona and corona the reaction rate is much more rapid because the energy is more fully expended in ionizing the gases instead of being wasted in getting through the glass wall, as in the Siemen's tube. However, this is not pure gain in the production of liquid because the solid formed in the corona types of discharge is equal in weight to the liquid. The solid hydrocarbons deposit on the glass (or metal) wall in a gummy adherent coating. Their average molecular weights remain unknown as no solvent has been found for them. Free carbon also forms on the metal electrodes in small tree-like deposits. Its amount is, however, relatively small, as will be seen in Table VIII.

In the present work eleven semi-corona tubes of pyrex glass (Fig. 1) were connected in series as to gas flow but in parallel as to electrical flow. The eleven central electrodes of $^1/_8$-inch aluminum rod were connected in parallel to an A. C. source (Thordarson transformer) with 18,000 volts on the secondary. The discharge took place across the annular space of 0.5 inch to the outer glass wall of the tubes, all of which were immersed in an electrolytic solution (sodium carbonate) which was grounded, thus constituting the other electrode. The solution was heated to 70° for the purpose of causing the first liquid droplets formed on the wall to flow off to the trap more readily, thus avoiding production of liquids of high viscosity and molecular weight by continued action of the

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[1] This paper includes part of an investigation of "The Effect of Electrical Discharge upon Gaseous Hydrocarbons," Project No. 8 of American Petroleum Institute Research. Financial assistance has been received from the research fund of the American Petroleum Institute, donated by the Universal Oil Products Company. This fund is administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project No. 8.

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[4] S. C. Lind and George Glockler, (I) *Trans. Am. Electrochem. Soc.*, *52*, 37–46 (1927); (II) THIS JOURNAL, 50, 1767–1772 (1928).

[5] S. C. Lind and D. C. Bardwell, *ibid.*, **48**, 2335–2351 (1926).

discharge on the liquid already formed (see Paper II). All eleven traps were cooled to a common low temperature suitable to each gas (Table VIII), to cause condensation and to prevent further ionization in successive tubes of heavy gas molecules which would give a still denser liquid. Gas samples were taken from beyond the last discharge tube from time to time. The liquid products were drawn off separately from each tube by cutting its fine glass tip. Solid products were removed (with difficulty) from the wall of each tube after the system had been cut apart.

The entire reaction takes place in a closed glass system (pyrex) out of access to air, so that products containing only hydrogen and carbon were obtained. The first experiment using the series flow apparatus (Fig. 1) was made with propane. These results will be described in detail, and the same procedure and apparatus were used with the other hydrocarbons, methane, ethane, butane and ethylene, data for which are also given in this paper.

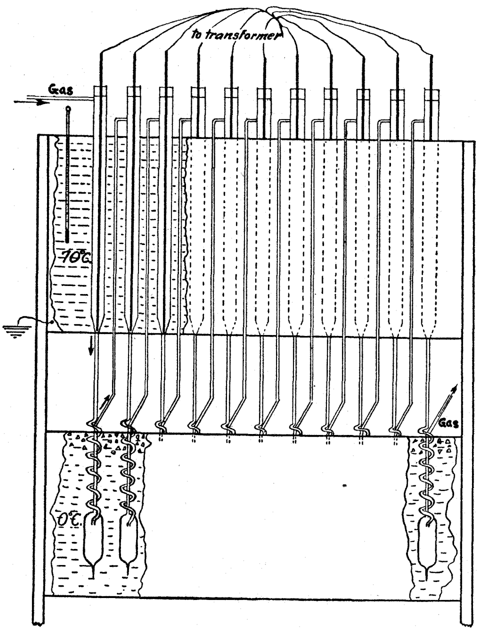

Fig. 1.—Semi-corona apparatus series gas flow.

Propane. Experiment No. 1.—In this experiment no heater was used for the discharge tubes, as it was hoped that the electrical energy applied would maintain their temperature at 60–70°. Actually the sodium carbonate electrolyte surrounding these tubes and hence controlling the temperature of their outer walls, in which we were most interested, would heat only to 35°. The accumulation of liquid in the traps being open to observation, the run was ended when any trap first became full of liquid, in this case the last one, No. 11. By collecting a sample of gas of definite volume and then condensing all gases in the sample at liquid-air temperature, only hydrogen and methane are left. Since they are always the principal gaseous products (Paper I), the course of the reaction can be followed by determining their combined partial pressure. The following data show how the reaction gradually became slower in the whole system, due to the

TABLE I

DECREASE IN REACTION RATE DUE TO DEPOSITION OF SOLID ON THE GLASS WALL

EXPERIMENT NO. 1 WITH PROPANE

Time	Pressure, mm.	Remarks
2–14–28	299.3	Partial pressure of reaction products, $H_2 + CH_4$, after condensing C_3H_8 and other gases from one atmosphere of total pressure.
2–15–28	320.0	
2–17–28	270.0	
2–21–28	180.0	

decrease in efficiency of each tube owing to the deposition of the solid hydrocarbons on the wall, which diminishes the current and hence the ionization and chemical action in each tube.

The distribution of liquid products in successive tubes in the series is shown in Table II. The total yield of liquid in this experiment was **37.09** g. from 550 g. of propane, using 51.5 kw. hours.

Properties of **Liquid** Condensates.—The following properties have been determined for the liquid condensate of each tube: index of refraction for sunlight at 21°, density, average molecular weight and the color (arbitrary scale of the Union oil colorimeter).

TABLE II

LIQUID HYDROCARBON CONDENSED FROM PROPANE IN INDIVIDUAL TRAPS IN ELEVEN SEMI-CORONA SERIES SYSTEM. FIRST EXPERIMENT

Trap no	Yield of liquid product, g	Av. mol. wt.	Density	Index of refrac. 21° n_{Sun}	Color (Union Oil Colorimeter)	Glass wall thickness (inches)
1	0 372	183.1	0.8393	1.4673	7.88	0.0359
2	0.739	157.5	.8062	1.4573	4.25	.0329
3	1 276	139.9	.7882	1.4512	2.75	.0334
4	1 500	138.7	.7872	1.4499	3.32	.0360
5	4 030	145.7	.7894	1.4486	4.50	.0306
6	3 349	126.7	.7814	1.4450	3.44	.0346
7	4 780	130.4	.7672	1.4400	3.38	.0365
8	4 056	118.0	.7658	1.4380	3.00	.0312
9	4 548	114.0	.7540	1.4315	1.94	.0301
10	5 056	109.3	.7611	1.4326	1.82	,0315
11	8.997	133.9	.7827	1.4454	4.67	.0380
	36.699					
12[a]	0.391	115.1	.7424	1.4300	.06	..
	37.090					

[a] The twelfth trap was not related to any ozonizer. It was an additional condensation **trap,** placed at the exit end of the apparatus. Its purpose was to catch any condensable material not caught in the eleventh trap.

The properties given in Table II are shown graphically in Fig. 2. It should be remembered that the liquids are all very complex. No efforts to fractionate them will be reported in the present paper. All data refer to the liquids as obtained.

Correlation of **Properties.**—Inspection of the curves of Fig. 2 shows at once that index of refraction, density, average molecular weight and color are all correlated properties and hence show similar curves when plotted in the order of the successive traps. All four properties show a marked fall when proceeding in the direction of flow. Irregularities are probably due to accidental variations in individual tubes, either wall thickness or eccentricity of the central electrode.

This fall in average molecular weight, etc., is closely but inversely related to the yield per trap. The greater the yield per tube, the faster the flow of liquid from the walls, hence the shorter the time of exposure to further discharge which has already been shown (Paper II) to be the cause of *high* condensation, average molecular weight, color, density, viscosity, etc.

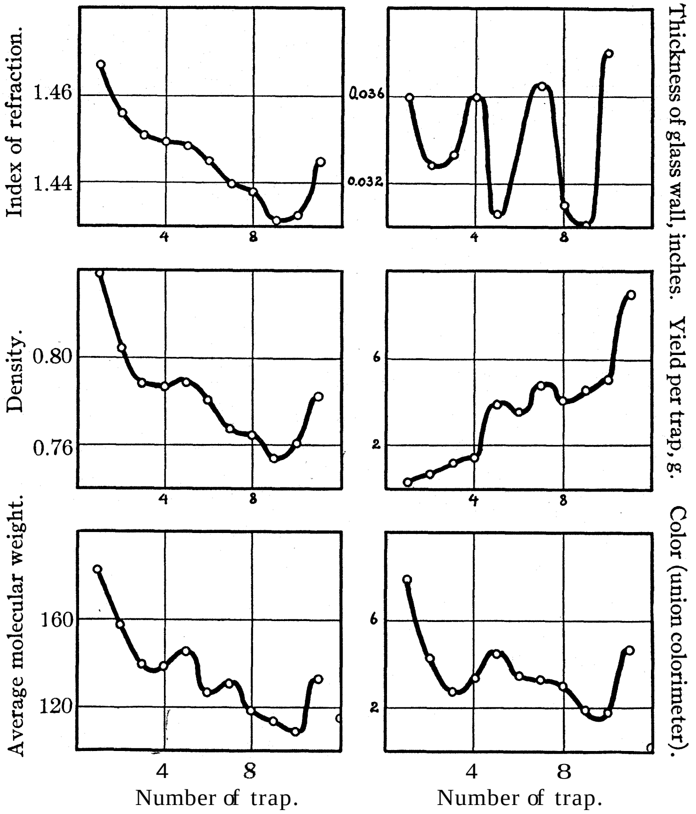

Fig. 2.—First propane run—eleven semi-coronas in series.

In order to demonstrate more clearly the correlation of index of refraction to density and to molecular weight, the data of Run No. 1 with propane have been plotted in two curves (Fig. 3). These curves have been used to obtain the density and molecular weight of the liquid product of other gaseous hydrocarbons from their indices of refraction. The agreement with values found directly by the freezing point lowering in benzene was fairly satisfactory, as is seen in Fig. 5, where the double circles show the actual check determinations in comparison with the predicted curves.

Yield per Tube.—As has just been seen the yield per trap increases on passing to successive tubes in the direction of gas flow. Three causes are to be considered: (1) a purely physical inefficiency or lag in vapor condensation, which would give an increased concentration in later tubes, further augmented by electrical generation of new condensable vapor. This effect might not be expected to increase through many tubes but to reach a steady state; however, it should be remembered that presumably the more of heavy molecules reaching a given tube, the easier it is to produce ionization there and hence more of the condensable product is formed. *(2)* The carrying over to higher tubes of molecules already condensed (chemically) but not sufficiently so to condense physically to liquid. These heavy readily ionized molecules also supplement the yield. (3) *A delayed chemical condensation* exists, as demonstrated in Paper II, p. 1771. All three of these effects work in the same direction to give more liquid in successive tubes. It is not now possible to evaluate the influences separately. It is evident that there would be a limit to this increase though it is not reached in this case, but is in propane Run 2, where, on account of a slower rate of flow and consequent earlier depletion of reactant gas, a maximum is passed. The conversion of total propane to liquid product is only 6.7% in Run 1 (see Table VII).[6]

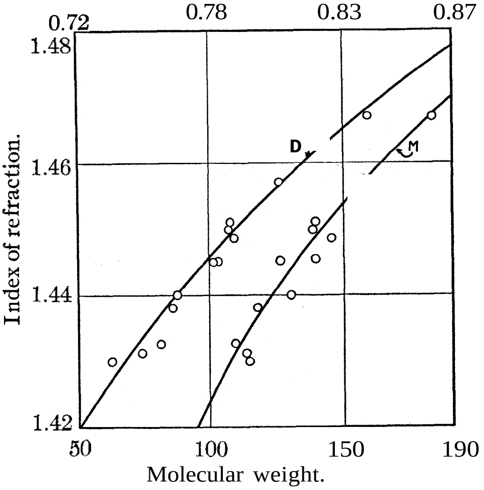

Fig. 3.—Molecular weight and density as functions of index of refraction. First propane run in eleven semi-corona apparatus.

TABLE III

EXPERIMENT NO. 1 ON PROPANE. ANALYSIS OF INITIAL AND EFFLUENT GASES

Initial gas		Effluent gas	
Permanent gases	0 12%	$H_2 + CH_4$	26.06%
C_2H_6	0 51	C_2H_6	7.05
C_3H_8	99 12	C_3H_8	64 50
C_4H_{10} (and higher)	0.42	C_4H_{10} (and higher) by difference	2.39
Total	100.17	Total	100.00

Solid Deposits.—The glass walls were covered with a resinous inert solid deposit of the character already described, the amount of which was

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[6] The efficiencies given always refer to the amount of initial gas sent through the apparatus. The efficiency of the ozonizers decreased during the experiments (see Tables I and IV) and it was not possible to calculate the actual amount of initial gas used from the gas analysis.

not determined in this run. The aluminum rod electrodes had a deposit of carbon in tree-like formation, the amount of which was relatively small but undetermined (compare Table VIII).

Propane. Experiment 2.—The same sample of gas was used as in Experiment 1, and the same apparatus (Fig. 1), the chief difference being that the rate of flow was reduced from 1.45 in Run 1 to 0.54 liters per hour in Run 2. Due to this slower rate of flow, a number of differences are observed owing to the more rapid depletion of propane, as may be seen by comparing the following with corresponding data for Run 1.

TABLE IV

DECREASE IN REACTION RATE DUE TO DEPOSITION OF SOLID ON THE GLASS WALL

EXPERIMENT 2

Time	Pressure, mm.	Remarks
3-2-28	396.0	Partial pressure of reaction products, H_2 + CH_4, after condensing C_3H_8 and other gases from one atmosphere pressure.
3-5-28	320.0	
3-10-28	220.0	

Owing to the higher utilization of propane (60% to solid and liquid against 6.7% to liquid or 13% estimated for liquid and solid in Run 1) the yield per trap passes a maximum at the eighth tube and then falls off in the ninth, tenth and eleventh (Fig. 4 and Table V). The data are given in Table V and plotted in Fig. 5. Inspection of the latter shows the same kind of correlation between index of refraction and color as in Run 1, and in addition a close correlation, almost equality, between the

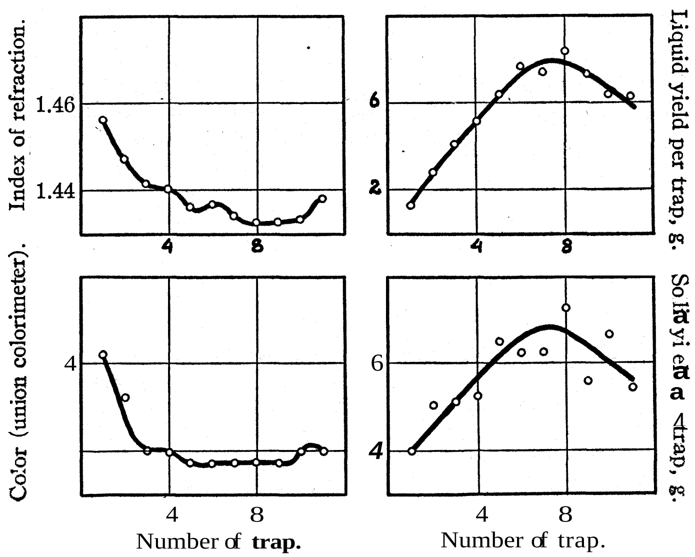

Fig. 4.—Second propane run—eleven semi-coronas in series.

amount of solid and liquid product, though the distribution per tube is somewhat different.

TABLE V

SECOND EXPERIMENT ON PROPANE CONDENSATION IN ELEVEN SEMI-CORONA APPARATUS

Trap	Yield of liquid, g	Index of refraction, 21° n_{Sun}	Color of liquid (Union oil colorimeter)	Yield of solid on glass wall, g.
1	1.315	1.4663	4.25	4.03
2	2.896	1.4472	3.25	5.09
3	4.118	1.4415	2.00	5.15
4	5.150	1.4403	2.00	5.29
5	6.432	1.4362	1.75	6.50
6	7.648	1.4370	1.75	6.20
7	7.431	1.4342	1.75	6.26
8	8.355	1.4327	1.75	7.28
9	7.158	1.4328	1.75	5.62
10	6.390	1.4334	2.00	6.69
11	6.328	1.4380	2.00	5.47
12[6]	0.200	1.4352	0.00	
	63.42			63.64

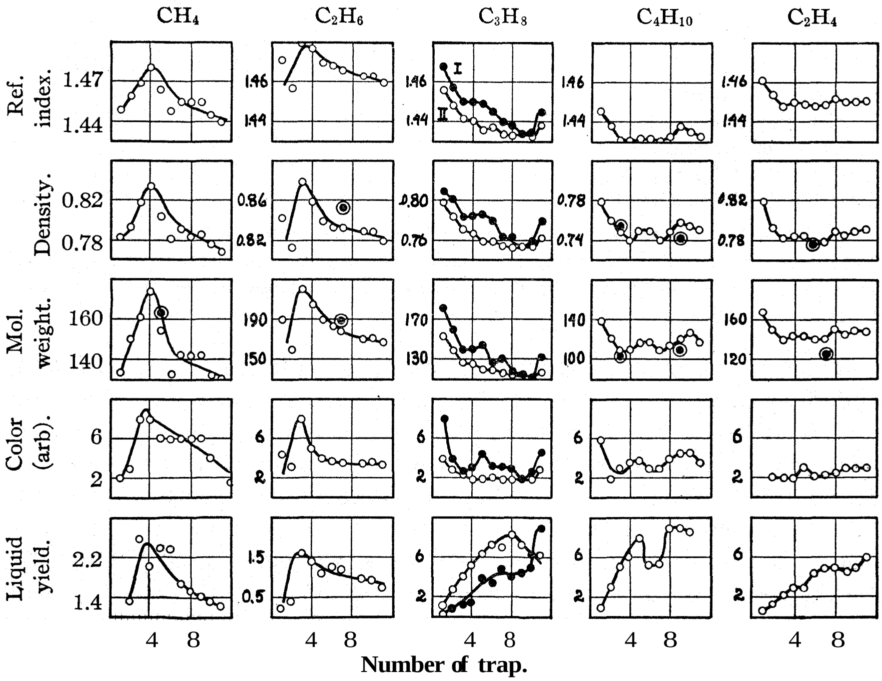

Fig. 5.—Properties of liquid condensates obtained from gaseous hydrocarbons in semi-corona discharage.

TABLE VI

EXPERIMENT NO. 2 ON PROPANE. ANALYSIS OF INITIAL AND FINAL GASES

Initial gas, %		Effluent gas, %	
Permanent gases	0.12	$H_2 + CH_4$	45.00
C_2H_6	0 51	C_2H_6	9.78
C_3H_8	99.12	C_3H_8	41.60
C_4H_{10} (and Higher)	0.42	C_4H_{10}	2.90
		C_5H_{12}	1.63
Total	100.17	Total	100.91

Table VII contains a summary and comparison of the principal results for Propane in Runs 1 and 2.

TABLE VII

COMPARISON OF EXPERIMENTS 1 AND 2 ON PROPANE

	Run 1	Run 2
Rate of flow in liters per hour	1.45	0.514
Time of experiment, days	9	10
Amount of propane used, liters (N.T.P.)	280	111
Amount of propane used, g.	550	218
Kw. hours used	81.5	63.42
Secondary volts	18,000	18,000
Molecular weight of liquid product range	183–115	160–120
Yield of liquid product, g.	37.09	63 42
Density of liquid oil	0.8392–0.7424	0.82–0.75
n_{Sun}^{21}	1.4673–1.4300	1.4563–1.4352
Solid deposit on glass wall, g.	[a]	63.64
Efficiency of conversion to liquid, %	6.7	29.0
Efficiency of conversion to liquid and solid, %	[a]	58.5
Liquid per kw. hour, g.	0.455	0.480
Liquid and solid per kw. hour, g.	[a]	0.985

[a] The solid deposit was not determined in Propane Run 1, because it was first discovered there while attempting to clean the apparatus. In cleaning the apparatus with hot chromic acid copious evolution of carbon dioxide from the wet oxidation of the solid on the wall was noticed.

Results for Other Hydrocarbons—Methane, Ethane, Propane, Butane and Ethylene.—Having in the foregoing part of this paper given and explained in considerable detail the results obtained using propane as initial gas, the results for the four other hydrocarbon gases studied can be rather briefly summarized, as they are quite similar in most respects to those obtained for propane.

The eleven tube semi-corona apparatus was again used. All of the hydrocarbons examined give liquid condensates of the same general character. The relation between index of refraction, molecular weight and density is the same for the different liquid condensates, which is interpreted to mean that these liquids are all of the same type. This is supported by our ability to deduce their densities and molecular weights from their indices of refraction by using the corresponding curves from propane. Moreover, all of the condensates have a similar terpene-like odor. The results for all five gases are summarized in Table VIII.

TABLE VIII

COMPARISON OF EXPERIMENTS WITH FIVE GASEOUS HYDROCARBONS IN THE ELEVEN SEMI-CORONA APPARATUS. CENTRAL ALUMINUM ELECTRODE ($^1/_8''$ DIAM.) IN PYREX TUBES (2.0 CM. DIAM. AND 1 MM. WALL THICKNESS)

	Methane	Ethane	Propane, Run 2	Butane	Ethylene
Flow, l./hr.	0.57	0.45	0.514	0.60	8.58
Temp. of trap, °C.	0	0	0	10	0
Time, days	5.1	1.5	10	5.7	12.4
Gas used (N.T.P.), l.	64.0	14.9	111	74.1	155
Gas used, g.	45.7	19.9	218	192	193
Volts (secondary)	18,000	18,000	18,000	18,000	18,000
Primary kw. hrs.	102.7	15.7	132.0	63.4	196.3
Yield of liquid, g.	18.25	9.74	63.42	71.10	40.10
Mol. wt. of liq. **prod.**	130–170	170–210	120–160	110–140	130–160
Density of liq. prod.	0.78–0.83	0.81–0.87	0.75–0.82	0.74–0.78	0.78–0.82
n^{20}_{Sun}	1.44–1.46	1.46–1.48	1.42–1.47	1.43–1.45	1.45–1.46
Solid on glass wall, g.	4.4	0.1	63.64	(70.0)	78.6
Carbon on Al **rod, g.**	0.25	0.1	1.00	1.00	0.75
Eff. of conv. **(g. liquid)/** (g. gas used), %	40	48	29	37	21
G. (liq. + solid)/(g. **gas used), %**	50	48	58.5	73.5	61.4
G. liquid/kw. **hour**	0.178	0.62	0.48	1.09	0.204
G. (liquid + solid) per kw. hour	0.22	0.625	0.985	2.23	0.605

Discussion of Results

The results for propane, butane and ethylene were obtained under quite comparable conditions. This is not equally true of the experiments with methane and ethane, for which the runs were of much shorter duration due to premature failure of the glass under discharge with the result that formation of solid on the walls had only begun; consequently the clean tubes appear unduly efficient with respect to yield of liquid per unit weight of methane or ethane used or per unit of electrical energy applied to them, in comparison with results for the other gases.

Of course, the most satisfactory basis of comparison of the reaction yields for the different hydrocarbons would be in terms of yield per ion-pair; but since the ionization can neither be measured nor calculated,[7] we must be content with relative rather than absolute comparisons. It has been shown that the reactions have the same general character as those produced in the same gases by alpha radiation, and are presumably due to ionization. In the case of ozone formation by high-speed cathode rays,

[7] Lind, *Trans. Am. Electrochem. Soc.*, **53,** 26 (1928).

Busse and Daniels[8] have recently made a satisfactory estimate of the ratio (yield/ion pair) by assuming the total energy reaching their reaction vessel to be wholly expended in producing oxygen ions. Since such a large proportion of energy in the semi-corona discharge is lost to the wall, we cannot make their assumption. It appears more plausible to assume that so much of our energy is lost to the wall that the condition is more like that of alpha particles in vessels so small that all alpha particles cross the entire gas space, and that at the same pressure the amount of reaction in different gases is proportional to the product of the specific ionization yield per ion pair (M/N)—a comparison similar to the one made[9] for the results of Hutchinson and Hinshelwood[10] for the decomposition of NH_3 and N_2O in different tubes under conditions of equal current flow. It is not implied that any single electron traverses the entire gas space, but that under conditions of equal electron flow the total ionization and chemical action in the different gases will be relatively in the proportion given by the product:[11] ks $\times$ M/N where *ks* is Bragg's specific (molecular) ionization and M/N is the yield of molecules M reacting per N ion pairs.

Two assumptions are involved: (1) that the relative specific molecular ionization by electrons is the same as by alpha particles, which seems by far more plausible than to assume, as has been sometimes done by others, that the probability of ionization by electrons is proportional to the number of molecules present, regardless of their size or nature; and (2) that the yield (M/N) is the same, or, more generally, that the chemical behavior of ions is the same, whether produced by bombardment by electrons or by alpha particles. If the ions produced are identical, this postulate must be true, other conditions being alike. Therefore, we should expect the relative yields to be roughly proportional to those shown for ks X M/N.

TABLE IX

THEORETICAL RELATIVE YIELDS OF LIQUID FROM DIFFERENT GASEOUS HYDROCARBONS UNDER ELECTRICAL DISCHARGE

Hydrocarbon	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4
ks[12]	1.01	1.97	3.05	4.02	1.65
M/N[12]	2.0	2.0	2.0	2.0	5.0
ks X M/N	1.0	1.95	3.02	3.99	4 08
Corrected	0.25	0.98	3.02	3.99	4.08

If by yield we mean *liquid* (and solid) formed, then the relative values for methane and ethane must be yet further reduced because in a reaction

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[8] F. W. Busse and F. Daniels, THIS JOURNAL, **50,** 3271–3286 (1928).

[9] S. C. Lind, *Trans. Am. Electrochem. Soc.,* 53, 31–32 (1928); *Science,* 67, 567–568 (1928).

[10] W. K. Hutchinson and C. N. Hinshelwood, *Proc. Roy. Soc. London,* **117A,** 131–136 (1928).

[11] S. C. Lind, "Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Company, Inc., New York, **1928,** 2d ed., pp. 36 and 102.

of simple doubling such as $2CH_4 = C_2H_6 + H_2$ and $2C_2H_6 = C_4H_{10} + H_2$, neither of the gases can reach a condensable stage in a single step but must be acted on again (C_4H_{10} once and C_2H_6 twice), so that perhaps the actual relative values would be improved by dividing that for C_2H_6 by two and that for CH_4 by four. The higher numbers from propane up can all reach the liquid stage by a single doubling.

Some general resemblance, at least to the order given above, can be seen by inspecting the yields per kw. hr. or also per gram of gas used (Table VIII), but the picture is a very distorted one on account of the differences in the amount of solid on the different tubes, which as already mentioned was practically absent for CH_4 and C_2H_6 on account of the short time for accumulation. Hence, the relative yields from ethane and methane appear higher than they should; on the other hand, that of ethylene is depressed on account of the abnormal amount of solid formed.

It may appear strange that all of the hydrocarbons in spite of the great differences in their densities, molecular weights, etc., give liquids of about the same properties with respect to density, average molecular weight, etc. Striking as this may appear on first thought, it is a simple consequence of multiple doubling and of the experimental arrangement so as to arrest further doubling by condensing the product in low temperature traps outside of the zone of reaction. By changing the temperature of the discharge region and of the traps, the properties of the liquids could be varied at will, and all of the liquids brought to equal molecular weights of some other value in an arbitrary manner.

The authors wish to thank Mr. J. L. Wilson, who has assisted in this work as American Petroleum Institute Research Assistant.

Summary

1. Like ethane, the other lower hydrocarbons, methane, propane, butane and ethylene condense to liquid and solid hydrocarbons in semi-corona discharge (central aluminum rod in a (pyrex) glass cylinder).

2. The condensation of saturates is brought about by the elimination of hydrogen and some methane as under alpha radiation.

3. In series gas flow through a number of discharge tubes, the amount of liquid condensate increases in successive tubes. If the rate of flow be so slow that depletion of reactant becomes considerable, then a maximum of liquid yield is attained in an intermediate tube.

4. The liquid products obtained from different hydrocarbons or in different tubes from the same hydrocarbon are similar in physical properties, when obtained at the same trap temperature.

5. The liquid products are very complex. Fractionation was not attempted in the present work.

6. Solid hydrocarbons are obtained in slight amount in the Siemens

tube, in larger quantity equal to that of liquid in the corona tubes. The solid is gummy or resinous, inert toward solvents and chemical reagents except strong oxidizing reagents.

7. In corona discharge a small amount of free carbon is deposited on the metal electrode in tree-like formation.

8. A close correlation of index of refraction, molecular weight, density, color and viscosity characterizes all the liquid products. Increase in all these properties is inversely proportional to the *yield,* for which a simple explanation is given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MIDDLEBURY COLLEGE]

OXIDATION OF BENZOINS TO DIKETONES WITH IODINE

BY BEN B. CORSON AND ROBERT W. MCALLISTER

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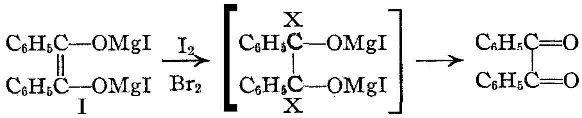
Benzoin, anisoin, piperoin, furoin, etc., are easily oxidized to the corresponding diketones by various methods. On the other hand, the conversion of aliphatic analogs of benzoin such as butyroin, $C_3H_7CHOHCOC_3H_7$, into diketones is not so convenient. We have studied the oxidizing effect of iodine, thinking that the reaction might be applicable to aliphatic acyloins. Solid aromatic acyloins were used in the investigation since they are easier to manipulate than the liquid aliphatic analogs. Although the reaction seems of no value in the preparation of aliphatic diketones, some of the results which came to light are of general interest.

The reaction is based on a recent observation of Gomberg and Bachmann[1] that benzil results from the action of iodine or bromine on stilbenediolate (I).



$$\begin{matrix}C_6H_5C\text{—}OMgI\\ \| \\ C_6H_5C\text{—}OMgI\end{matrix} \xrightarrow[Br_2]{I_2} \left[\begin{matrix} X\\ C_6H_5C\text{—}OMgI\\ | \\ C_6H_5C\text{—}OMgI\\ X\end{matrix}\right] \longrightarrow \begin{matrix}C_6H_5C{=}O\\ |\\ C_6H_5C{=}O\end{matrix}$$

I

We have obtained 90–95% yields of benzil by the addition of iodine to alkaline solutions of benzoin. Benzoin was dissolved in methyl alcohol and sodium methylate was added, followed by iodine. Due to the extreme sensitiveness to oxidation of an alkaline solution of benzoin, the reaction mixture must be protected from air. This was accomplished either by working in an atmosphere of dry nitrogen or by keeping the alcohol solution boiling throughout the duration of the reaction. Similar yields of diketone (80 to 90% of the theoretical amount) were obtained from anisoin, piperoin and furoin.

It seems quite likely that the mechanism of this reaction is that described by Gomberg, namely, the removal of sodium from the dienolic

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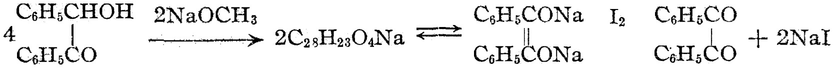
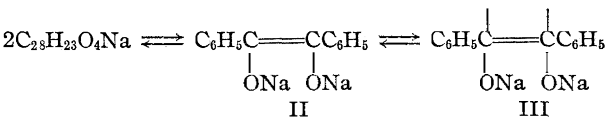
[1] Gomberg and Bachmann, THIS JOURNAL, 49,2584 (1927).

salt. However, the interaction of benzoin with sodium methylate does not yield stilbenediolate, as would be required for the above mechanism. According to Meisenheimer,[2] the product is a white salt which contains one atom of sodium per two molecules of benzoin, $C_{28}H_{23}O_4Na$. If our suggested mechanism be correct, this salt must be in equilibrium with disodium stilbenediolate.



$$4\begin{matrix}C_6H_5CHOH\\ |\\ C_6H_5CO\end{matrix}\xrightarrow{2NaOCH_3}2C_{28}H_{23}O_4Na \rightleftharpoons \begin{matrix}C_6H_5CONa\\ \|\\ C_6H_5CONa\end{matrix}\quad I_2\quad \begin{matrix}C_6H_5CO\\ |\\ C_6H_5CO\end{matrix} + 2NaI$$

A deep reddish-purple color appears immediately when sodium methylate is added to a methyl alcohol solution of benzoin. When a small amount of iodine is added, the color quickly fades to straw yellow, but in a few moments the purple color returns. Also, the admission of a small amount of air discharges the color but the original purple color quickly reappears when air is prevented from entering. Gomberg[1,3] observed a similar behavior with his unsaturated halomagnesium glycolates. He suggests that the remarkable reactivity of the latter may be due to a partial opening of the double bond. These color changes could be explained in the same manner.



$$2C_{28}H_{23}O_4Na \rightleftharpoons \underset{\text{II}}{C_6H_5\underset{ONa}{\underset{|}{C}}=\underset{ONa}{\underset{|}{C}}C_6H_5} \rightleftharpoons \underset{\text{III}}{C_6H_5\overset{|}{\underset{ONa}{\underset{|}{C}}}=\overset{|}{\underset{ONa}{\underset{|}{C}}}C_6H_5}$$

The color would be due to the free valented form (III); iodine or oxygen momentarily removes it from the equilibrium. Whatever may be the significance of the color of an alkaline solution of benzoin, it nevertheless serves as a delicate test for the latter.

Experimental Part

Oxidation of Benzoin—At first the oxidation reaction with sodium methylate and iodine was carried out in air but the benzil was always impure. In order to discover what impurities might result due to air, we carried out the following run. Twenty-one grams of benzoin was dissolved in 500 cc. of hot methyl alcohol and 7.5 g. of sodium, dissolved in 100 cc. of methyl alcohol, was added. Considerable light purplish solid separated from the dark solution. The mixture was heated to ±50° for half an hour and mechanically stirred while a stream of compressed air was blown into the flask. The solid finally disappeared; the solution was still dark colored at the end of the half hour. We isolated 2 g. of benzil and 12 g. of benzoic acid, which accounts for 60% of the original benzoin. When the oxidation of benzoin with methylate and iodine was run in an atmosphere of dry nitrogen or in boiling methyl alcohol, pure benzil was obtained in 90 to 95% yields. The conditions are described in the preparation of furil. The methyl alcohol must be free from acetone, ethyl alcohol, etc., else iodoform will contaminate the product.

Oxidation of **Furoin.**—Ten grams of furoin was dissolved in 225 cc. of boiling methyl alcohol and to the boiling solution was added a hot, freshly prepared solution of

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[2] Meisenheimer, Ber., 38,874 (1905); cf. Garner, *Am. Chem.* J.,32,583 (1904).

[3] *Cf.* Hantzsch and Glower, Ber., 40,1519 (1907).

sodium methylate made by dissolving 2 5 g. (105% of the calculated amount, assuming the product to be a disodium derivative of dienol) of sodium in 50 cc. of pure methyl alcohol. To the boiling solution was then added, in three portions, 14 g. (106% of the calculated amount based on sodium) of iodine. The final color of the solution was brown. The heat was then removed; furil immediately began to crystallize. The mixture was allowed to cool to room temperature and filtered. A small additional yield was obtained by concentrating the mother liquor. The total yield of air-dried product, melting point 164–165° (corr.), was 8 g. (80% of the theoretical amount). The best solvent for crystallizing furil is benzene. Pure furil melts at 165 to 165.5° (corr.). When bromine is substituted for iodine, there is a resultant drop in yield of 20 to 30%.

Until recently the only practical preparation of furil was air oxidation of a cold alkaline solution of furoin as described by E. Fischer.[4] Recently a new method has been described by Nisbet[5] which involves the use of nitrobenzene as oxidizing agent.

In the oxidation of benzoin we used twice the amount of sodium methylate required to form stilbenediolate. This seemed to be the best amount. However, when this proportion of sodium was used with furoin, the yield of furil dropped 40%; with furoin the sodium methylate should be barely in excess.

Preparation of **Furoin.**—Furoin was prepared by Fischer's directions.[4] The purity of the crude product depends greatly upon the quality of the furfuraldehyde. If the latter is very impure, it is almost impossible to obtain pure furoin. We purified the crude product as follows. The crude furoin (dark brown and apt to be sticky) was air-dried and then allowed to stand for twelve hours in ether. It was filtered and then soaked in fresh ether for a second twelve hours, after which it was again filtered by suction. The ether removed a black tar. The furoin was dissolved in boiling ethyl alcohol (±150 g. per 500 cc. of alcohol) and precipitated by slowly pouring the hot alcohol solution into 5 volumes of water with rapid stirring. The solid was filtered, dissolved in alcohol and precipitated again with water. The process was repeated once more. The final product was of a light tan color and the supernatant aqueous alcohol from which it separated was clear and red. The first precipitation yielded a product which filtered slowly. However, the second and third precipitations gave a product which filtered very nicely. Finally, the furoin was crystallized from hot ethyl alcohol, filtered by suction, washed with ether and air-dried. Pure furoin melts at 138–139° (corr.).

Benzoin Color Test.—The purple color of an alkaline solution of benzoin has long been used as a color test for both benzoin and benzil,[6] but it has never been evaluated quantitatively. Using our procedure a positive color test is given by 0.0002 g. of benzoin and a weak test with 0.0001 g. This is one hundred times or so as sensitive as the test with Fehling's solution. Under the conditions of the test benzil alone gives no purple color even when the solution is warmed. However, benzil added to the test solution intensifies the benzoin color. The intensification is slight but it is unmistakable. This deepening of color would seem to be evidence of quinhydrone formation.[7]

The procedure consists in first adding to a 10-cc. test-tube 1 cc. of sodium methylate solution (4 g. of sodium in 50 cc of methyl alcohol), next 0.1 cc. of saturated benzil solution and, finally, anywhere from 0.02 to 1 cc. of the methyl alcohol solution of benzoin to be tested.

This color test can be applied to furoin and benzofuroin, the former giving a navy

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[4] Fischer, *Ber.*, **13,** 1334 (1880); **Ann., 211,** 214 (1882).

[5] Nisbet, *J. Chem. Soc.*, 3121 (1928).

[6] Liebermann and Homeyer, Ber., **12,** 1975 (1879); Bamberger, *ibid.*, 18, 865 (1885); Scholl, *ibid.*, **32,** 1809 (1899); Hantzsch and Glower, *ibid.*, 40, 1519 (1907).

[7] Scholl, *ibid.*, **32,** 1809 (1899).

blue with sodium methylate, the latter a delicate amethyst. In both cases the color is deeper in the presence of furil, benzofuril or benzil. On the other hand, neither piperoin nor anisoin give any color with methylate; neither does piperil nor anisil intensify the color of benzoins that do give color, namely, benzoin, furoin and benzofuroin.

Simple sugars are similar to benzoin inasmuch as they have a carbonyl group adjacent to hydroxyl. Levulose, however, does not respond to the color test; neither does butyroin, $C_3H_7CHOHCOC_3H_7$, a typical aliphatic acyloin.

We compared the delicacy of the color test against that of the Fehling test. The smallest amount of benzoin capable of yielding a significant precipitate of cuprous oxide in an hour was 0.01 g. An immediate color change on simple heating required 0.02 g. to 0.05 g. This is a poor test when compared with the color reaction with sodium methylate, which gives an immediate and conclusive purple color with 0.0002 g. of benzoin. The extreme limit of the Pehling test is 0.005 g. of benzoin. At this dilution the mixture must stand for two hours or more and the indication which finally results is very doubtful.

This work was aided by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. Various analogs of benzil can be prepared by iodine oxidation of alkaline solutions of the corresponding benzoins. A mechanism involving stilbenediolate is suggested.

2. The frequently described delicate color test with alcoholic alkali is shown to be applicable to certain benzoins but not to others. It is suggested that the color is indicative of trivalent carbon.

MIDDLEBURY, VERMONT

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 44]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. IX. THE VAPOR PRESSURES, DENSITIES AND REFRACTIVE INDICES OF CERTAIN BINARY MIXTURES

BY SPENCER W. PRENTISS

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In the seventh paper of this series the velocity constants of the reaction at 25° between pyridine and ethyl iodide in a number of solvents were presented. The relative values of the constants, indicating the adjuvance of the solvents, were as follows.

TABLE I

VELOCITY CONSTANTS

Benzene	1	n-Propyl alcohol	1.11
Nitrobenzene	25	*n*-Butyl alcohol	1.11
Acetone	12.8	Isopropyl alcohol	1.07
Methyl alcohol	2.5	*Sec.*-butyl alcohol	1.00
Ethyl alcohol	1.4	*Tert.*-butyl alcohol	**0.93**

In view of the differences in chemical behavior shown by benzene, *n*-butyl alcohol and *tert.*-butyl alcohol, it was regarded as noteworthy that these compounds possessed nearly the same adjuvance. It has been suggested that adjuvance may be related more to physical forces set up between the molecules involved than to chemical attractions.

The present investigation was undertaken to test the validity of this hypothesis. If physical forces are the important factor, it seemed to us that a study of the physical properties of several binary mixtures of each reactant with a few of the more adjuvant and less adjuvant solvents might yield significant results. Specifically, we hoped to show that the adjuvance of the solvent would bear a simple relation to the deviations, from ideal solution laws, of vapor pressures, densities and refractive indices of several binary mixtures of the solvent with each reactant. No simple relationship has been found which will apply to all the cases studied. However, it is felt that the data obtained in this study possess sufficient value, apart from the above-mentioned hypothesis, to warrant their publication.

During this investigation a simple apparatus has been devised for measuring the vapor pressures of liquid mixtures where only small quantities—5 cc. or less—are available for each determination. It is hoped that adaptations of this apparatus may also be found useful in other lines of work.

Vapor Pressures.—The vapor pressures at 20° were measured by a static method. A small glass ampoule containing 3 or 4 cc. of the liquid was broken in an evacuated space of small volume and the pressure developed was measured by means of a mercury manometer. In this way the vapor pressures of pyridine, ethyl iodide, two of the more adjuvant, and two of the less adjuvant solvents, together with those of several binary mixtures of each reactant with each solvent, were obtained.

A numerical expression of the deviation, when this is small, of the observed vapor pressures from Raoult's Law is given by the exponent A in the equations[1]

$$p_1 = p_1^\circ \mathrm{N}_1 \, e^{A\mathrm{N}_2^2} \tag{1}$$

$$p_2 = p_2^\circ \mathrm{N}_2 \, e^{A\mathrm{N}_1^2} \tag{2}$$

where p° is the vapor pressure of the component and p is its partial pressure over a solution in which its mole fraction is N. Where $A = 0$ the equations become the familiar expressions of Raoult's Law; positive and negative values of A correspond, respectively, to positive and negative deviations from the law.

The values of A, which when substituted in Equations 1 and 2 yielded values of $p_1 + p_2$ in fair agreement with the observed total vapor pressures, are given in Table II. In the first line are given the solvents studied

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[1] See Hildebrand, "Solubility," The Chemical Catalog Co., New York, 1924, p. 45.

and in Line 2 their relative adjuvance in the reaction under consideration, as found by the previous determination of velocity constants; Line 3 gives the A-values for the system solvent–pyridine, and Line 4 the A-values for the system solvent–ethyl iodide,

TABLE II

A-VALUES

Solvent	Nitrobenzene	Acetone	n-Butyl alcohol	Benzene
Adjuvance	25	12.8	1.11	1.00
***A*, Pyridine**	1 425	0 448	0.48	0.24
***A*, Ethyl iodide**	1.17	0.76	1.70	0.65

No simple combinations of the A-values for pyridine and ethyl iodide have been found which give values in any way proportional to the values found for the relative adjuvance.

Densities and Indices of Refraction.—The density and refractive index of mixtures of each reactant with nitrobenzene, acetone, *tert.*-butyl alcohol and benzene, respectively, were measured. In these instances, also, no parallelism was found between the adjuvance of a given solvent and the deviation of the measured property from the value it would have if the solution were ideal. In general the deviations were small and of opposite sign to those found in the measurements of vapor pressure. The data are given in Tables V and VI in the experimental part of this paper.

Experimental Part

The vapor pressures were measured in the apparatus shown in Fig. 1b, constructed of pyrex glass. Connections were made through Q to a Cenco Hyvac pump, through T to a Langmuir diffusion pump backed up by the Hyvac pump through R, through S to a McLeod gage and through J to a water-jet aspirator. The chamber, **O**, served to break the ampule containing the liquid under investigation. It was provided with a ground joint to permit the removal of the lower portion and to enable the latter to be turned in the fixed member. Inward pointing knobs were made, as close as possible to the top and bottom, by heating a very small spot to a bright orange and pushing in the hot spot with a small stout wire. This chamber, together with a stirrer and a Beckmann thermometer, was immersed in a water-bath contained in a Dewar flask. The water-bath temperature was controlled by a heating coil and a cooling-water tube (not shown) also immersed in the bath. The setting of the Beckmann thermometer was effected through the use of a thermometer reading from 0 to 40° which had been standardized by the Berliner Reichsanstalt. A paper scale was placed behind the manometer.

The vapor space from O and M to the mercury surface at P, approximately 30 cc., corresponded to $30/22{,}400 \times 273/293 = 0.0012$ mole. As the internal diameter of the manometer tube was approximately 0.4 cm., the vapor space was increased by $0.4^2\pi/2 = 0.25$ cc., corresponding to 0.000010 mole for each centimeter of pressure. The corrections to be subtracted from the weights of each component taken were obtained by multiplying the number of moles of vapor, as above determined, by an approximate value of the pressure fractions, p_1/p and p_2/p, respectively.

Ampules having a capacity of about 4 cc. were made from 10 mm. o.d. soft glass tubing (Fig. 1a). The tip **A** was made quite fragile, and the shank D fairly heavy, with an internal diameter of 2 or 3 mm. A 5-cc. pipet was drawn out at the tip into a small tubule, about 0.5 mm. i.d., 1 mm. o.d., and 10 cm. long; by passing this tubule down the shank of the ampule, the latter could be filled with a liquid without wetting any part of the ampule above the level C.

A determination of the vapor pressure was carried out in the following manner. The desired mixture was first made up by weight, using a 5-cc. glass-stoppered weighing bottle. Enough of this was transferred to the ampule to bring the liquid to the level C, just above the shoulder. By bringing the tip of the tubulated pipet into contact with the inside wall of the ampoule and letting the liquid flow in very slowly at first, the tip A could be filled with liquid without entrapping any air.

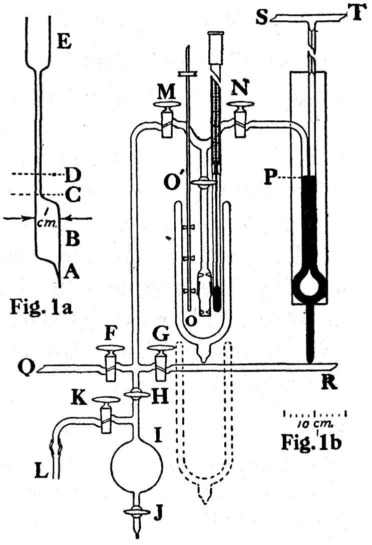

Fig. 1.

The ampule was next attached by means of the rubber tubing L, to the Bulb I, which had been previously exhausted by means of a water-jet aspirator to a pressure of from 5 to 10 mm. of mercury. The ampule and contents were chilled by immersion in ice and concentrated hydrochloric acid, Stopcock K was opened and the ampule was sealed off at a point near the top of the shank, using a hand torch. The remaining long portion of the shank was removed by sealing at a point D such that when the ampule was subsequently placed in the chamber O the upper tip would project above the upper knobs without touching the wall directly above them.

The ground joint was next very sparingly greased, the ampule placed in the lower portion with the fragile tip resting on the bottom and the chamber put together as at O (ampule not shown), with the Dewar flask lowered. The right side of the manometer having been previously evacuated to less than 0.01 mm. as shown by the McLeod gage, the rest of the apparatus was evacuated through Q as far as Stopcocks H and G, until there was no further change in the level of mercury in the left arm that could be seen with the unaided eye.

Stopcock O' was next turned so as to break the lower tip of the ampule, whereupon the liquid ran out into the chamber. The Dewar bath was placed in position and Stopcock M was closed; whereupon Stopcock O' was slowly opened by a minute amount until the bulk of the vapor had formed, when it was opened wide. After the establishment of equilibrium, shown by repeatedly and slowly approaching the temperature, 20°, alternately from above and below, the vapor pressure was read and recorded.

Tables III and IV give the data thus found. Table III gives the vapor pressures of the individual components, in mm. of mercury, observed at 20.00°. In Table IV, Cols. 1 and 2 give the number of moles, X 100, of each component in the solution, as determined by weight; Col. 3 gives the mole fraction, N_2, of pyridine or ethyl iodide, corrected for vaporization; Cols. 4 and 5 give, respectively, the observed vapor pressure and that calculated from Equations 1 and 2, using the value of *A* given in the table for each system.

TABLE III

VAPOR PRESSURES OF THE COMPONENTS

									Average
Pyridine	17.4	21 0	21 5	22 7	19.9	21.2	22.3	22 0	21.0
Ethyl iodide			115.2	115.8	118.8	117.0	118.3		117.0
Nitrobenzene					0.0				0.0
Acetone				194.0	195.7	195.3			195 0
n-Butyl alcohol				12.2	13.3	14 3			13 3
Benzene				84.0	85 0				84 5

TABLE IV

EXPERIMENTAL DATA

Solvent, $n_1 \times 100$	Reactant, $n_2 \times 100$	N_2	p, obs., mm. of Hg	p, calcd., mm. of Hg
Nitrobenzene–Pyridine. $A = 1.425$				
1.00	4.00	0.79	19.1	17.7
2.00	3.00	.59	16.4	15.7
240	160	.38	13.6	13.8
3.21	081	.18	11.0	9.9
3.20	0.81	.18	8.5	9.9
Nitrobenzene–Ethyl Iodide. $A = 1.17$				
1.00	4.00	.79	100	97.5
1.00	4.00	.79	99	97.5
2.00	3.01	.58	85	84.0
2.70	180	.37	68	69.0
2.70	1.80	.37	68	69.0
3.60	0.90	.17	45	44.6
3.60	0.90	.17	45	44.6
Acetone–Pyridine. $A = 0.448$				
1.30	3.91	.77	73	75.0
2.50	2.50	.52	118	118.0
2.00	2.02	.53	118	116.5
3.31	1.10	.26	156	155.5
Acetone–Ethyl Iodide. $A = 0.76$				
0.50	4.50	.91	142.5	140.0
1.50	3.51	.71	169.0	171.5
2.50	2.50	.51	186.0	188.5
3.20	1.60	.34	196.0	196.0
4.00	1.00	.20	199.0	199.0
5.00	0.29	.05	1965	196.5
n-Butyl Alcohol–Pyridine. $A = 0.48$				
1.00	4 00	0.799	21.5	20.71
1.00	4.02	.799	20.5	20.71
1.07	3.74	.775	20.5	20.67
2.50	2.51	.500	19.5	19.34
2.50	2.50	.500	19.5	19.34
400	1.00	.200	16.5	16.55
4.03	1.01	.195	16.0	16.49
n-Butyl Alc.–Ethyl Iodide. $A = 1.70$				
1.00	4.00	.795	111.5	107.9
1.01	4.00	.795	109.5	107.9
1.00	4.00	.795	106.5	107.9
2.00	4.00	.660	104.5	103.5
2.00	3.00	.590	105.0	1018
2.00	3.00	590	104.5	101.8
2.50	2.50	.480	101.0	99.2
2.50	2.50	.480	99.0	99.2
3.01	2.50	.425	95.0	97.7
3.00	2.00	.380	92.0	96.3
4.00	1.00	.170	69.0	75.7
Benzene–Pyridine. $A = 0.65$				
1.00	4.00	.81	39.0	42.0
2.00	3.00	.61	56.0	56.1
3.00	2.00.	.41	69.0	66.4
4.00	1.01	.21	77.0	75.3
Benzene–Ethyl Iodide. $A = 0.24$				
1.00	4.00	.80	113	114.0
2.00	3 00	.60	109	109 6
3.00	2.03	.40	104	103 6
4.24	1.06	.20	96	95 6

Densities and Refractive Indices.—The densities of the pure components had been measured with especial care using a Sprengel pyknometer, yielding values which are believed fairly to indicate the degree of purity of the substances used (see below). However, for the purpose of comparing the densities of the binary mixtures studied, all that was required was a rapid, fairly accurate method which would give reproducible results. A pyknometer patterned after that described by Mulliken[2] was found to fulfil these requirements perfectly. Accordingly, the densities of the mixtures were measured and those of the pure components remeasured, at 25.0°, using this instrument. No excessive care was used in its calibration and no buoyancy corrections have been included in the density values as given. Nevertheless, it is evident from an inspection of the data that the main purpose of the density measurements—namely, a determination of the deviations from ideal solution laws—has been adequately fulfilled.

The refractive indices were measured at the same temperature, 25.0°, using an Abbé refractometer. The density and refractive index of the pure components and of 2 to 1 and 1 to 2 molecular mixtures of each reactant with each solvent were measured. The mixtures were made up by volume, in duplicate, and the number of moles of each component was calculated using the observed density of the latter. One determination of each property of each mixture was made. The agreement in the case of the pure components was within 1 or 2 units in the last decimal, for both properties. From the respective property and the mole fraction of each pure component were calculated the molecular volume and the molecular refraction of ideal solutions having the composition indicated, using the formulas

$$MV = \frac{1}{D}(M_1N_1 + M_2N_2), \text{ and } MR = \frac{n^2 - 1}{n^2 + 2} \times MV$$

where MV = molecular volume, MR = molecular refraction, D = mass/volume at 25.0°, M = molecular weight, N = mole fraction and n = refractive index at 25.0° using the D line. Tables V and VI give the data thus found.

TABLE V

EXPERIMENTAL DATA

Compound	*M*	*D*	MV	*n*	MR
Pyridine	79.1	0.975	81.2	1.5044	24.06
Ethyl iodide	156.0	1.922	81.2	1.5076	24.18
Nitrobenzene	123.1	1.200	102.6	1.5476	32.58
Acetone	58.1	0.781	74.4	....	...
Tert.-butyl alcohol	74.1	.781	94.9	....	...
Benzene	78.1	.871	89.7	1.4950	26.18

The materials used were of the best grade obtainable and were further purified before use. Pyridine was refluxed with quicklime, ethyl iodide with silver powder and lumps of marble, and they were then fractionally

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[2] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 229.

TABLE VI

RESULTS OF EXPERIMENTS

Solvent, cc.	Reactant, cc.	N_2	LJ	MV, obs.	*MV*, calcd.	*n*	*MR*, obs	*MR*, calcd.
Nitrobenzene–Pyridine								
1.55	2.45	0.67	1.062	88.4	88.3	1.5166	26.78	26.88
1.55	2.45	.67	1.059			1.5180		
2.86	1.14	.33	1.134	95.6	95.6	1.5339	29.68	29.79
2.86	1.14	.33	1.136			1.5325		
Nitrobenzene–Ethyl Iodide								
1.55	2.45	.67	1.685	86.5	88.3	1.5307	26.70	26.96
1.55	2.45	.67	1.665			1.5278		
2.86	1.14	.33	1.404	95.7	95.6	1.5371	29.90	29.83
2.86	1.14	.33	1.398			1.5380		
Acetone–Pyridine								
1 24	2 76	.67	0.918	78.5	79.0			
1.24	2.76	.67	.918					
2.58	1.42	.33	.852	76.2	76.7			
2.58	1.42	.33	.854					
Tert.-butyl Alcohol–Pyridine								
1.47	2.53	.67	.904	85.6	85.7			
1.47	2.53	.67	.903					
2.79	1.21	.33	.840	90.2	90.4			
2.79	1.21	.33	.841					
Benzene–Pyridine								
1.42	2.58	.67	.943	83.4	84.0	1.5013	24.57	24.74
1.42	2.58	.67	.943			1.5016		
2.75	1.25	.33	.908	86.2	86.9	1.4987	25.30	25.47
2.75	1.25	.33	.907			1.4985		
Benzene–Ethyl Iodide								
1.42	2.58	.67	1.551	84.1	84.0	1.5007	24.78	24.82
1.42	2.58	.67	1.540			1.5012		
2.75	1.25	.33	1.193	86.8	86.9	1.4965	25.38	25.51
2.75	1.25	.33	1.202			1.4968		

distilled. Nitrobenzene was repeatedly frozen and distilled *in vacuo.* Acetone from the bisulfite compound was first refluxed with permanganate, then repeatedly with anhydrous carbonate of potash and then fractionally distilled. The alcohols were purified in general by the procedures used in this Laboratory in previous investigations. Benzene (thiophene free) was shaken with concentrated sulfuric acid, alkali and water, then refluxed with sodium and distilled from flasks containing this metal.

Table VII gives the physical constants of the materials used. The figures represent the maximum and minimum values of the constants for the different compounds used, and not the variation in the property for the individual compound. The boiling range, for example, was usually 0.1 or 0.2° for 90% distilled.

TABLE VII

PHYSICAL CONSTANTS OR MATERIAL

	d_4^{25}	M. p., °C.	B. p. (760 mm.), °C.
Pyridine	0.9775 to 0.9779	....	115.2 to 115.4
Ethyl Iodide	1.922 to 1.924	....	72.2 to 72.4
Nitrobenzene	1.197 to 1.199	5.7 to 5.8	
Acetone	0.7855 to 0.7863	....	56.1 to 56.3
n-Butyl alcohol	0.8058 to 0.8060	....	117.7 to 117.8
Tert.-butyl alcohol	0.7807	24.5	82.5 to 82.6
Benzene	0.8730 to 0.8736	5.4[a]	80.1 to 80.3

[a] The melting point was not determined for all the samples used.

The author is indebted to Professor J. F. Norris for his continued interest in this work, and to Professor George Scatchard for many helpful suggestions and criticisms, and especially for indicating the applicability of the Duhem–Margules equations to the problem in hand.

Summary

1. The vapor pressures of several binary mixtures of nitrobenzene, acetone, n-butyl alcohol and benzene with pyridine, and with ethyl iodide, have been measured at 20° by a static method.

2. The densities of similar mixtures of nitrobenzene, acetone, *tert.*-butyl alcohol and benzene with pyridine, and of nitrobenzene and benzene with ethyl iodide, and the refractive indices of mixtures of nitrobenzene and benzene with pyridine and with ethyl iodide, have been measured at 25°.

3. For the reaction between pyridine and ethyl iodide an attempt has been made to show that the adjuvance of the solvent, reported in paper No. VII of this series, would bear some relation to the deviation, from ideal solution laws, of vapor pressures, densities or refractive indices of binary mixtures of the solvent with each reactant. No such correlation, however, has been observed.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

THE ISOMERIC ALPHA,BETA-DIPHENYLGLUTARIC ACIDS[1]

BY S. AVERY AND W. D. MACLAY

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Part I. The Optically Inactive Acids

Introduction

An acid of this group was first synthesized by Avery and McDole[2] through the addition of benzyl cyanide to cinnamic ester and the hydrolysis of the product formed. The acid crystallized as needles. The corrected melting point was 226–228°. In this paper it will be referred to as "the higher-melting acid." The possibility of the presence of a lower-melting isomeric acid formed along with the higher-melting acid was considered by Avery and McDole in a discussion, of which the following is an abbreviation: "By working over the mother liquors a substance was obtained melting at 205" (uncorr.). However, careful work showed the presence of a small amount of nitrogen in the supposed isomeric acid and when this compound was placed in a sealed tube with hydrochloric acid and heated, the compound obtained in every case was the diphenylglutaric acid melting at 224° (uncorr.)." The nitrogen just referred to was actually due to a very minute trace of the monoamide of diphenylglutaric acid.[3] The 205" compound was in reality the nearly pure isomeric glutaric acid to be described in this paper as "the lower-melting acid," the melting point of which is 208–210° (corr.). It forms nearly square or oblong flat plates, beveled plates or prisms. The crystals formed under different conditions vary considerably in superficial appearance.

Substituting phenylacetic ester for phenylacetonitrile (benzyl cyanide), Borsche[4] effected the synthesis of the higher-melting acid. He describes a very satisfactory method for preparing the esters of this acid, and the acid itself, but makes no mention of the lower-melting acid which is formed in considerable quantity when the ester of the higher-melting acid is hydrolyzed by potassium hydroxide in the usual way.

By oxidizing 1,2-diphenylcyclopentene-3, Kishner[5] obtained a mixture of acids which he converted into their methyl esters and separated by fractional distillation. He thus obtained a methyl ester melting at 87° having the same percentage composition as the known methyl ester (143°) of α,β-diphenylgutaric acid. By saponifying this ester he obtained an

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[1] Read at the meeting of the Division of Organic Chemistry, American Chemical Society, Columbus, May 1, 1929.

[2] Avery and McDole, THIS JOURNAL, 30,596, 1423 (1908).

[3] Avery, *ibid.*, SO, 2516 (1928).

[4] Borsche, *Ber.*, 42,4496 (1909).

[5] Kishner, J. Russ. *Phys.-Chem. Soc.*, 47, 1819–1848 (1915).

acid in the form of needles melting at 200–201°, which he called the maleinoid form, designating the higher-melting acid as the fumaroid form.

By oxidizing β,γ-diphenylvalerolactone, Meerwein and Dott[6] obtained in the form of prisms an acid melting at 203–204°. It formed a methyl ester apparently identical with the "maleinoid" ester of Kishner. The acid, however, with its higher melting point and different crystalline form does not closely correspond to the latter's "maleinoid" acid.

The investigators referred to were in fairly close agreement in so far as the higher-melting acid is concerned. All reported needles melting above 220°, the exact temperature depending on the rapidity of heating. All reported a methyl ester melting sharply at about 143°. On the other hand, the only close agreement in regard to the lower-melting acid is the fact that two of the investigators report a methyl ester melting at 87°.

In view of the uncertainty in regard to the lower-melting acid, the authors of this paper regarded a thorough study of the subject as desirable.

Experimental Part

The Anhydride of the Lower-Melting Acid.—Five grams of the higher-melting acid was heated in a sealed tube with approximately 10 g. of acetyl chloride at 140° for four hours. The product of the reaction was treated with 50 cc. of petroleum ether. An oil separated out and became crystalline on stirring. After an hour the crystals were filtered off; yield, 4 g. The anhydride was purified by recrystallizing from hot tertiary amyl alcohol and gave plates, m. p. 124°, by dissolving in chloroform, adding absolute alcohol and condensing in a current of cold, dry air; by dissolving in chloroform and precipitating with petroleum ether, m. p. 126.5°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3. Found: C, 76.6; H, 5.4.

That this body is the anhydride of the lower-melting acid is shown by its reacting readily to form this acid (and its esters), and not the higher-melting acid from which it was prepared. It also deports itself as an anhydride in forming the acid amide, the imide and the anilic acid.

This anhydride was formed almost quantitatively by treating the lower-melting acid with an excess of acetyl chloride, evaporating on the steam-bath and allowing the residue to crystallize.

The Lower-Melting α,β-Diphenylglutaric Acid.—This acid is gradually formed when the anhydride just described is treated with boiling water. It is formed more readily by dissolving the anhydride in an alkaline carbonate solution and precipitating with strong acid. It was first isolated in pure condition, however, by the following method: 30 g. of the methyl ester, m. p. 143°, was saponified by boiling with 15 g. of potassium hydroxide in 100 cc. of 95% alcohol. As the potassium salt precipitated out, water was added and the boiling continued for two hours. The solution was then evaporated to dryness, dissolved in water and added gradually to an excess of a 10% solution of hot hydrochloric acid. After cooling, the white crystalline mass was filtered off and washed well with water; yield, approximately 25 g. This was dissolved in hot 95% alcohol; boiling water was then added to incipient turbidity. On cooling, needles of the nearly Pure higher-melting acid separated; yield, approximately 15 g. The filtrate was condensed to about one-third of its previous volume and cooled. The mix-

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[6] Meerwein and Dott, *J. prakt. Chem.*, 97, 264–268 (1918).

ture of the higher and lower acids formed was then filtered off; yield of mixed acids, approximately 10 g. The needles of the higher-melting acid and the beveled plates or short prisms of the lower-melting acid appeared to be present in about equal amounts when seen through the microscope. About 1 g. of the pure lower acid was obtained by repeated recrystallization from dilute acetic acid.

For practical purposes, however, the mixed acids are converted into the pure anhydride by heating with acetyl chloride at 140°. The anhydride in turn passes readily into the pure lower-melting acid as has just been stated.

The lower-melting acid formed by the oxidation of 1,2-diphenylcyclopentene-3 as described by Kishner, but purified by dissolving out the benzoic acid with benzene and recrystallizing the residue by dissolving in as small an amount of ethyl acetate as possible, adding benzene and condensing in a current of dry, cold air, is readily obtained in a pure condition.

The three samples just described have the same crystalline form, the same solubility relations and the same melting point, 208–210° (corr.). Melting points of mixed samples showed no variation.

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.8; H, 5.7. Found: C, 71.6; H, 5.7. Titration: 0.1225 g. required 8.6 cc. of $N/10$ NaOH. Calcd.: 8.6 cc.

Except for the higher melting point obtained, the results just given are so closely in agreement with the conclusions of Meerwein and Dott that the synthesis of the acid by their method for the sake of comparison seemed unnecessary.

The Monoamide of α,β-Diphenylglutaric Acid.—Two grams of the anhydride dissolved in chloroform was treated for some time with dry ammonia gas. The white powder formed suspended in chloroform was shaken with concentrated ammonium hydroxide solution and evaporated to dryness. The residue recrystallized from 50% alcohol melted at 200–205° with decomposition and the evolution of ammonia. It was found to be identical with the monoamide of diphenylglutaric acid from β,γ-diphenyl-γ-cyanobutyric acid.[3] This fact is of interest as indicating that the cyano derivatives through which Avery and McDole first synthesized the higher-melting acid belong to the series of the lower-melting acid and that the series of the higher-melting acid is reached only in the final hydrolysis.

The Imide of the Lower-Melting α,β-Diphenylglutaric Acid.—The monoamide of the lower-melting acid on boiling with a mixture of 95% alcohol and concd. hydrochloric acid gives the corresponding imide as coarse, hair-like crystals; m. p. 225–229° without evolution of ammonia.

The imide may also be made as follows: β,γ-diphenyl-γ-cyanobutyric methyl ester is treated with strong alcoholic potash and evaporated almost to dryness over the open flame. Water is added and the process repeated. The mass is then dissolved in glacial acetic acid, concd. hydrochloric acid added and it is again evaporated over the open flame till a mass of coarse, hair-like crystals separate out. More hydrochloric acid is added, the mass again concentrated, then diluted with water, filtered and washed; yield, nearly quantitative. Recrystallized out of 80% alcohol it melts at 225–229°.

Anal. Calcd. for $C_{17}H_{15}O_2N$: C, 76.9; H, 5.7; N, 5.3. Found: C, 76.8; H, 5.6; N, 5.2.

The Anilic Acid.—2.26 g. of the anhydride of the lower-melting α,β-diphenylglutaric acid was dissolved in benzene, 0.93 g. of aniline in benzene was added and the solution warmed. A crystalline precipitate formed which after heating at about 80° for ten minutes was filtered off and washed with benzene; the yield of the crude product was nearly quantitative. Recrystallized three times from 50% alcohol, the anilic acid showed a constant melting point of 201–202°. The crystals appeared in the form of needles or rods.

Anal. Calcd. for $C_{23}H_{21}O_3N$: C, 76.8; H, 5.9; N, 3.9. Found: C, 76.5; H, 5.8; N, 3.8. Titration: 0.109 g. required 3.0 cc. of *N*/10 NaOH. Calcd.: 3.0 cc.

Transformation: The Higher Series $\rightleftarrows$ the Lower.—Concentrated hydrochloric acid diluted with an equal volume of water appears not to change compounds of the higher into those of the lower-melting series at any temperature,

Below 150° cyano derivatives are hydrolyzed by hydrochloric acid to a mixture of the amide and the lower-melting acid; at 150° to a mixture of the two acids, the higher-melting acid predominating as the temperature rises.

Below 180° the esters of the lower acid are hydrolyzed by hydrochloric acid with little transformation. Above 180° esters of the lower acid (and at 200° the acid itself) are transformed more or less completely into the higher-melting acid.

Saponification by alcoholic potassium hydroxide leads to the corresponding acid, mixed, however, with a varying amount of the isomeric compound. This action appears to explain why Kishner on saponifying the pure (87°) lower-melting methyl esters secured needles melting at 200–201°. He appears to have isolated a mixture of the acids.

As Kishner pointed out, the lower-melting acid is in part transformed into the higher by heating above its melting point.

The method of proceeding from the higher (or mixed acids) to the lower through the anhydride route has made it possible to prepare the lower-melting acid in quantity without excessive cost and effort.

Optical Properties.—Both acids are optically inactive.

Summary to Part I

The work previously published on the higher-melting acid, in so far as this paper relates to it, is confirmed in all essential points.

The lower-melting acid has been prepared in a pure condition by different methods, its crystalline habit noted and its melting point determined.

A mixture of the higher and lower-melting acids has been separated by fractional crystallization.

The higher-melting acid has been transformed into the anhydride of the lower. This anhydride has been isolated in pure form and used practically in preparing the lower acid.

The methyl ester (m. p. 143°), the ethyl ester (m. p. 93.3°) and the acid (m. p. 226–228°) belong to what we have termed the higher-melting series; the methyl ester (m. p. 87°), the ethyl ester 76° (as pointed out by Kishner) and the acid (m. p. 208–210") belong to the lower-melting series.

The cyano and monoamide derivatives,[7] the imide (m. p. 225–229°) and the anilic acid (m. p. 201–202") described in this paper, also appear to be members of the lower melting series.

To use the phraseology sometimes employed, but generally accepted with mental reservations when applied to saturated dibasic acids, the members of the higher-melting series might be termed "*trans*" or "fumaroid" compounds; while those of the lower-melting series would be designated as "*cis*" or "maleinoid" forms. Though these terms are freely used in the literature of the dimethyl- and diethylglutaric acids, they help to classify rather than to explain this and similar cases of stereoisomerism. Hence in

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[7] Avery, THIS JOURNAL, 50, 2515–2516 (1928).

the hope of throwing more light on the real difference in stereo structure between the two series, the authors next undertook to resolve each acid into its optical isomers.

Part II. The Optically Active Acids

Introduction

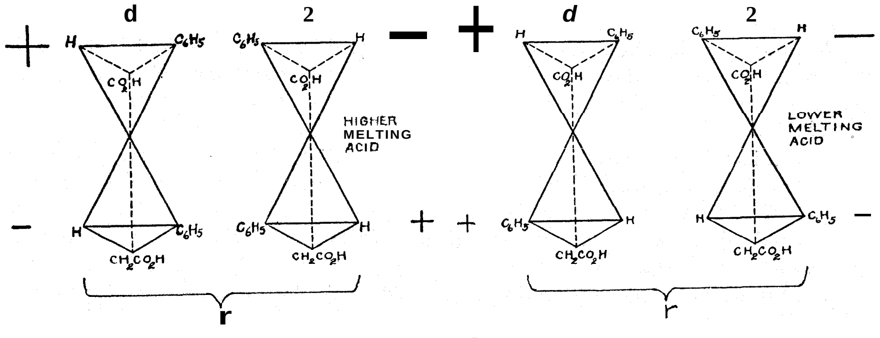
The general formula of all isomeric α,β-diphenylglutaric acids, $HOOCCH_2CH(C_6H_5)CH(C_6H_5)COOH$, shows two asymmetric carbon atoms of unequal effect on polarized light. The α-atom has without question the greater capacity for specific rotation.[8] Indicating this optical difference by the size of the signs employed, we have the following possibilities

$$HOOCCH_2CH(C_6H_5)CH(C_6H_5)COOH$$

$$\left.\begin{array}{lcc} d & \text{\Large$+$} & - \\ l & \text{\Large$-$} & + \end{array}\right\} r \qquad \left.\begin{array}{lcc} d & \text{\Large$+$} & + \\ l & \text{\Large$-$} & - \end{array}\right\} r$$

The higher-melting acid (m. p. 226–228°), as the experimental part of this paper will show, has been resolved, through fractional crystallization of the brucine salt, into isomers, one showing a d-rotation of 58.7°, and one showing a similar l-rotation.

The lower-melting acid (m. p. 208–210°) has also been resolved into isomers, one showing a l-rotation of 140.7°; the other showing a d-rotation of approximately the same amount. Hence it follows that the higher-melting acid (m. p. 226–228°) is a racemic form of the $\text{\Large$+$}\ -$; $\text{\Large$-$}\ +$ type. The lower 208–210° acid is a racemic acid of the $\text{\Large$+$}\ +$; $\text{\Large$-$}\ -$ type. The conclusion is then that there are in all six isomers, two inactive and four active. These may be expressed in another way, as indicated.



Experimental Part

Resolution of the Higher-Melting Acid.[9]—Thirty grams of finely powdered α,β-

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Compare $C_6H_5CH(OH)COOH$, +157°, Ber., 37,3176 (1904), with $C_6H_5CH(OH)CH_2COOH$, 4-19, *ibid.*, 39, 790 (1906).

Compare Wren and Still, *J. Chem. Soc.*, 107,444 (1915).

diphenylglutaric acid (226–228°) was thoroughly mixed with 82.8 g. of anhydrous brucine and stirred with 6000 cc. of water on a boiling water-bath until practically all of it had gone into solution. The temperature of the solution was kept below 80°. After filtration, the solution was allowed to cool. At the end of four days the crop was filtered and allowed to dry on a porous plate; yield, 67.5 g.

This material was recrystallized from hot water, 30 cc. of the solvent being used for each gram of the salt. The course of the resolution was followed by determining the specific rotation of the acid obtained from the successive filtrates. The values for the rotations of these filtrates made in acetone solution were as follows: −12.5°, −4.2°, +36.3°, +45.4°, +50.6°, +56.4°, +57.0°.

The crop from which the last filtrate was obtained, consisting of long well-defined prisms with pointed ends and weighing 5.5 g., was dissolved in hot water and decomposed with hydrochloric acid. 1.5 g. of *d*-α,β-diphenylglutaric acid was isolated, the specific rotation in acetone solution being as follows: $[\alpha]_D^{20}$, +58.7° (1 g. in 25 cc. of soln. gave, in a 1-dcm. tube, +2.35°). The rotation of this acid remained unchanged after further recrystallization.

d-α,β-Diphenylglutaric acid crystallizes from dilute ethyl alcohol in fine, hair-like crystals with a melting point of 224–226°. It is slightly soluble in hot water and benzene, and exceedingly soluble in ethyl alcohol, methyl alcohol, acetone and ethyl acetate. The solubilities shown by this acid are much greater than those of the inactive acid.

The brucine salt of the *l*-α,β-diphenylglutaric acid being more soluble than the salt of the *d*-α,β-diphenylglutaric acid, the usual difficulties were encountered in obtaining the acid in a pure form. However, a levorotatory acid that was practically pure was obtained in the following manner: the filtrate from the first crop of brucine salt was concentrated under reduced pressure to 3000 cc. and allowed to crystallize. The crop was filtered, the filtrate concentrated to 1000 cc. in the same way and again allowed to crystallize; 34 g. of the crude levorotatory brucine salt was thus obtained. This salt was recrystallized from hot water until when viewed through the microscope it was found to be uniform in crystalline structure. The crystals were short, well-formed prisms with beveled edges. The crop was dissolved in water and decomposed with hydrochloric acid. The acid was recrystallized from dilute ethyl alcohol and gave a specific rotation in acetone solution as follows: $[\alpha]_D^{20}$, −58.0° (0.172 g. in 25 cc. soln. gave in a 1-dcm. tube −0.40°). The rotation of this acid remained unaltered with further recrystallization.

l-α,β-Diphenylglutaric acid recrystallizes from dilute ethyl alcohol in fine hair-like crystals similar to those of the d-acid. It also exhibits solubility properties analogous to those of its antipode. The melting point of the l-acid was slightly lower than that of the d-acid.

Racemization of the Active Acids.—Equal quantities of the d- and *l*-α,β-diphenylglutaric acids were placed together and recrystallized several times from dilute ethyl alcohol. The acid crystallized in long needles with a melting point of 226–228°. It was optically inactive and exhibited all the properties of the acid from which its component parts were originally derived.

Resolution of the Lower-Melting Acid.—The procedure was in general similar to that employed in resolving the isomer. The brucine salt of the l-acid first separates out in the form of diamond-shaped plates. On condensing the mother liquor after the plates have been filtered off, the brucine salt of the d-acid appears in the form of prisms.

Twenty grams of the impure plates containing a small percentage of prisms and some coloring matter was dissolved in 5% alcohol, boiled with charcoal and filtered. On cooling, colorless plates nearly free from prisms separated out. These were dissolved again in hot dilute alcohol and permitted to crystallize. The process was repeated about twenty times from dilute alcohol and finally several times from water until samples of acid recovered from successive filtrates showed no change in rotation.

The acid was recovered from the filtrates by condensing to a small volume, acidifying with hydrochloric acid, extracting with ether and recrystallizing from very dilute alcohol slightly acidulated with acetic acid.

The samples of acid from the first few filtrates appeared as prisms, then as scales without definite form and later as flattened needles. The specific rotation passed rapidly with the successive recrystallizations from +12° to −130°, still more slowly to −140°, where it remained practically constant. There now remained 5 g. of the brucine salt, which was converted into the acid and recrystallized from dilute alcohol slighty acidulated with acetic acid.

l-α,β-Diphenylglutaric acid thus prepared gave a specific rotation in acetone as follows: $[\alpha]^{20}_{D}$, **−140" (1.0 g.** in **25** cc. of soln. gave in a 1-dcm. tube **−5.63").** It crystallizes from hot dilute alcohol or acetic acid as long, flattened needles; m. p. 202°. The solubilities shown by this acid are much greater than those of the inactive acid from which it was resolved.

Titration of the E-acid: **0.1006** g. required **7** cc. of $N/10$ NaOH. Calcd.: **7.1** cc.

The corresponding d-acid was prepared as follows: **10** g. of the brucine salt, mostly prisms, previously mentioned as coming from the first filtrate after the first crop of diamond-like plates had been filtered off, was recrystallized from water until an admixture of diamond-shaped plates could no longer be detected by the microscope.

At this point the filtrates from the later recrystallizations were in turn decomposed and recrystallized as in the case of the I-acid. This process was repeated until a specific rotation of about +140° was observed in several successive samples. These latter samples were in turn recrystallized from dilute alcohol containing a drop of acetic acid. The d-acid thus obtained recrystallized in long flattened needles giving a melting point of **202".** *d*-α,β-Diphenylglutaric acid thus prepared gave a specific rotation in acetone as follows: $[\alpha]^{20}_{D}$ +140.6° **(0.2188** g. **in 25** cc. of solution gave in a **1-dcm.** tube **+1.23").**

Titration of the d-acid: 0.1848 g. required **12.9** cc. of $N/10$ NaOH. Calcd.: **13 ce.**

The I-acid recrystallized with an equal weight of the d-acid showed all the properties of the 208–210° form from which the 1- and the d-acid were resolved.

Acknowledgments.—To Dr. F. W. Upson we are especially indebted for suggesting the resolution, into their optical isomers, of the acids under consideration and for constructive criticism. Mr. R. M. Sandstedt has rendered us the favor of making the nitrogen determinations. Mr. Clifford Carr has greatly assisted in laboratory work generally and has made the combustions and titrations.

Summary of Part II

Both of the stereoisomeric acids considered in Part I have been resolved into optically active acids. Names for the six acids, now all definitely known, are suggested as follows.

PROPOSED NAMES

For the higher-melting acid (226–228°)		For the lower melting acid (208–210")	
$\alpha d,\beta l$ − $\alpha l,\beta d$-Diphenylglutaric acid (*i*), the r form of		$\alpha l,\beta l$ − $\alpha d,\beta d$-Diphenylglutaric acid (i), the r form of	
$\alpha d,\beta l$-Diphenylglutaric acid	(*d*) and	$\alpha l,\beta l$-Diphenylglutaric acid	(*l*) and
$\alpha l,\beta d$-Diphenylglutaric acid	(*l*)	$\alpha d,\beta d$-Diphenylglutaric acid	(*d*)

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

A STUDY OF THE POSSIBLE INTERCHANGE OF RADICALS ON HEATING A MIXTURE OF AN R'X AND AN RMgX COMPOUND

BY HENRY GILMAN AND HAROLD L. JONES

RECEIVED MAY 27, 1929 PUBLISHED SEPTEMBER 5, 1929

Introduction

In connection with studies on the comparative reactivity of RX compounds toward magnesium in ether, combinations of two RX compounds have been allowed to compete for a quantity of magnesium insufficient to react with both halides.[1] It would be necessary to assume in such studies that there is no interchange of radicals, as follows

$$\mathrm{RX} + \mathrm{Mg} \longrightarrow \mathrm{RMgX} \qquad \text{(I)}$$

$$\mathrm{R'X} + \mathrm{RMgX} \longrightarrow \mathrm{R'MgX} + \mathrm{RX} \qquad \text{(II)}$$

Obviously, if an interchange of radicals as illustrated in Reaction II occurred then the quantity of R'MgX compound formed would not be solely a measure of the rate of reaction between the R'X compound and Mg, but also a measure of any R'MgX compound that might have formed in accordance with Reaction II.

The assumption of no interchange of radicals appeared altogether reasonable prior to some studies by Gilman and Fothergill[2] on the probable dissociation of some Grignard reagents. Accordingly, the present study was undertaken to determine definitely whether the interchange pictured in Reaction II actually takes place under our particular experimental conditions. We have found that no such interchange of radicals occurs.[3]

The method used was to add carbon dioxide to a mixture of R'X and RMgX compounds subsequent to refluxing in an ether–toluene or ether–benzene mixture for a few hours. If no interchange took place, the acid formed after carbonation should be pure RCOOH. If some interchange occurred, then some R'COOH and RCOOH would result. In each of the several cases studied only one acid was obtained, namely, the acid corresponding with the RMgX initially present.

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[1] The results of another aspect of this problem have already been reported by Giman and Van der Wal, Bull. *soc. chim.*, *45* (1929). See, also, Rudd and Turner, *J. Chem. Soc.*, 687 (1928), and Gilman and Zoellner, THIS JOURNAL, 50, 2520 (1928)

[2] Gilman and Bothergill, *ibid.*, 51 (1929). An account of this investigation was presented at the May, 1929, meeting of the American Chemical Society held at Columbus, Ohio.

[3] We mean this statement to be confined to the specific combinations used in this study. We consider it likely that special combinations like triphenylmethylmagnesium chloride and bromotriphenylchloromethane will show an interchange. Studies of such combinations of R'X and RMgX compounds, each of which has a tendency to dissociate, are in progress.

Depending on the lability of the halogen in the R'X compound, a reaction takes place between the halide and the RMgX compound, as follows

$$R'X + RMgX \longrightarrow R'R + MgX_2 \qquad \text{(III)}$$

With some R'X compound, Reaction III goes to completion.[4] In order to have some RMgX present at the end of the preliminary refluxing with R'X, an insufficient quantity of the latter was used. The chief products obtained, therefore, were the RCOOH from the RMgX, and the RR coupling product. However, in the reaction between triphenylchloromethane, $(C_6H_5)_3CCl$, and phenylmagnesium bromide a very unusual product resulted, in addition to a small quantity of tetraphenylmethane, $(C_6H_5)_4C$, which would be expected in accordance with Reaction III. This unexpected product was obtained in a 47.4% yield and was identified as p-phenyl-triphenylmethane, p-$C_6H_5C_6H_4C(H)(C_6H_5)_2$. This compound was unexpected because it was not reported by a number of other investigators[5] of this particular reaction between triphenylchloromethane and phenylmagnesium halides. A study is in progress of this and related reactions concerned with the rearrangement of halides and organomagnesium halides,[6] and free radicals formed from them.[7]

Experimental Part

With the exception of triphenylmethylmagnesium chloride,[8] the Grignard reagents were taken from stock solutions of known titration value. The RMgX solutions were free from magnesium. After refluxing the ether–toluene or ether–benzene mixtures of RMgX and R'X compounds for about three hours and at a temperature of about 60°, the cooled mixture was treated with carbon dioxide after the procedure of Gilman and Parker.[9]

Subsequent to hydrolysis the acids were extracted with dilute alkali and then recovered in a customary manner by acidification. None of the acids was purified by crystallization. Instead the "crude acid" obtained directly on acidification (after carefully extracting the alkaline solution with ether to remove all non-acidic compounds) was dried to constant weight. With the acid obtained in this manner a melting-point

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[4] See Gilman and McGlumphy, Bull. *soc. chim.*, 43, 1322 (1929); Gomberg and Cone, ***Ber., 39,*** 1461 (1906); Spath, *Monatsh.*, 34, 1965 (1913). Together with Reaction III another coupling reaction can occur: $2RX + 2R'MgX \longrightarrow R{\cdot}R + R'{\cdot}R' + 2MgX_2$. This reaction has been discussed in detail by Fuson, THIS JOURNAL, 48, 830,2681,2937 (1926).

[5] Gomberg and Cone, ***Ber.,*** 39, 1461 (1906); Freund, ibid., 39,2237 (1906); Schmidlin, *ibid.*, 43, 1137 (1910); Meyer, *J. prakt. Chem.*, 82,521 (1910); Gomberg and Kamm, THIS JOURNAL, 39,2009 (1917); Gomberg and Forrester, *ibid.*, 47,2374 (1925).

[6] Gilman and Harris, *ibid.*, 49, 1825 (1927); Gilman and Kirby, *ibid.*, 51, 1571 (1929).

[7] Gilman and Fothergill, *ibid.*, 50, 3334 (1928); *ibid.*, 51 (1929); Gilman and Kirby, *ibid.*, 51, 1571 (1929).

[8] Prepared in practically quantitative yields by the method of Gilman and Zoellner, ***Rec. trav.*** *chim.*, 48 (1929).

[9] Gilman and Parker, THIS JOURNAL, 46,2816 (1924).

determination, a mixed melting-point determination with an authentic specimen and **a** neutralization equivalent were made.

Where the possible mixtures of acids were benzoic and phenylacetic acids (see the first two experiments in Table I) the method of mixed melting points is highly accurate. This was established by the melting-point determinations of a series of authentic mixtures of these two acids. From these preliminary melting-point determinations it was shown that *less* than 0.5% of either acid mixed with the other acid would give an unmistakable softening and depression of the melting point. This method of melting point of mixtures is not sufficiently sensitive with acids whose melting points are considerably removed from each other. An illustration is the third experiment given in Table I. In this case a distinctly high percentage of benzoic acid is required to depress the melting point of triphenylacetic acid. For this reason the purity of triphenylacetic acid was measured by the neutralization equivalent. Neutralization equivalents were also made of the acids in the fourth and fifth experiments (see Table I).

The non-acidic products were recovered in the usual manner from the ether–toluene or ether–benzene layer after alkaline extraction. These products were less carefully examined in this preliminary study because our chief interest was with the acids. Some details concerning the several experiments are given in the footnotes accompanying Table I.

TABLE I

REACTION BETWEEN R'X AND RMGX COMPOUNDS

		R'X								
		Used		Recovered						
		G.	Mole	G.	%	RMgX	Mole	RCOOH	G.	%
1	C_6H_5Br[a]	23.5	0.15	19.0	80	$C_6H_5CH_2MgCl$	0.25	$C_6H_5CH_2COOH$	15.2	44.7
2	$C_6H_5CH_2Cl$[b]	20.0	.15	14.0	70	C_6H_5MgBr	.25	C_6H_5COOH	10.6	34.7
3	C_6H_5Br[c]	4.0	.025	3.3	82.5	$(C_6H_5)_3CMgCl$	.04	$(C_6H_5)_3CCOOH$	6.1	51.2
4	$(C_6H_5)_3CCl$[d]	27.8	.1	..	..	$C_6H_5CH_2MgCl$	.25	$C_6H_5CH_2COOH$	3.2	9.4
5	$(C_6H_5)_3CCl$[e]	20	.072	..	..	C_6H_5MgBr	.25	C_6H_5COOH	11.6	38

[a] The phenylacetic acid obtained in this experiment melted at 77°, and a mixed melting-point determination with an authentic specimen of phenylacetic acid which melted at 77° showed no depression.

[b] The temperature during the three-hour period of heating was 64°. The benzoic acid obtained here melted at 121° and showed no depression in a mixed melting-point determination with an authentic specimen.

[c] This is the only experiment in which an ether–benzene mixture was used. In all others an ether–toluene mixture was used. Refluxing for three and one-half hours was carried out in an inert atmosphere by means of the special apparatus of Gilman and Hewlett, *Rec. trav. chim.*, 48 (1929). The neutralization equivalent of the triphenylacetic acid was 289; the calculated value is 288. There were also obtained 0.3 g. of triphenylcarbinol and 0.4 g. of triphenylmethane.

[d] A flocculent orange-colored precipitate formed on the addition of the Grignard solution, and the stirred and refluxed mixture later assumed an opaque light yellow color. The phenylacetic acid showed no depression in a mixed melting-point determination with an authentic specimen. Its neutralization equivalent was 137.6, whereas the calculated value is 136. There was also obtained 25.1 g. or a 75.2% yield of 1,1,1,2-tetraphenylethane, $(C_6H_5)_3CCH_2C_6H_5$.

[e] On the addition of the Grignard reagent the solution assumed a deep cherry-red color. The benzoic acid showed no depression in a mixed melting-point determination with an authentic specimen. Its neutralization equivalent was 120.1, whereas the calculated value is 122.

In addition there was obtained 0.2 g. or a 0.63% yield of tetraphenylmethane, the identity of which was confirmed by a mixed melting-point determination with an authentic specimen.

The non-acidic fractions also gave 10.9 g. or a 47.4% yield of *p*-phenyltriphenylmethane which after several crystallizations from hot absolute alcohol melted at 111°.

Anal. Calcd. for $C_{25}H_{20}$: C, 93.69; H, 6.31. Found: C, 93.20; H, 6.48. Mol. wt.: calcd., 320; found, 311.4.

The identity of this hydrocarbon was confirmed by a mixed melting-point determination with an authentic specimen melting at 111–112° and prepared in accordance with the directions of Schlenck, Weickel and Herzenstein, *Ann.*, 372, 18 (1909).

Summary

In connection with rate studies, series of mixtures containing an R'X and an RMgX compound have been heated to determine whether there is an interchange of radicals. No such interchange was observed. In the reaction between triphenylchloromethane and phenylmagnesium bromide an unusual product, p-phenyl-triphenylmethane, was obtained in a 47% yield.

AMES, IOWA

NEW BOOKS

Introductory Theoretical Chemistry. BY G. H. CARTLEDGE, Associate Professor of Chemistry, The Johns Hopkins University. Ginn and Company, 15 Ashburton Place, Boston, Massachusetts, 1929. xiv + 523 pp. 71 figs. 14 X 21 cm. Price, $3.60.

In the order of treatment, the author has followed the plan of his earlier "Inorganic Physical Chemistry."

Part I, pp. 1–202, The Nature of Matter, gives an interesting résumé of the historical development of the various laws relating to the gaseous, solid and liquid states. The kinetic theory, Avogadro's law, the determination of atomic weights, radioactivity, atomic structure and surface tension are carefully treated. Numerous examples and references are given to classical experiments, such as Black's quantitative study of chalk and lime, and Landolt's research into the conservation of mass. An abstract (7 pages) from "A Revision of the Atomic Weights of Sodium and Chlorine," Richards and Wells, serves to stimulate interest in original work.

Part II, pp. 203–294, deals with the nature of solutions. Here also the historical development is emphasized. Perfect solutions and Raoult's law are illustrated by the method of vapor pressure lowering. The molecular weight of dissolved substances is determined in accordance with the older ideas (van't Hoff factor *i*) instead of by application of modern thermodynamic methods. **A** whole chapter (16 pages) is devoted to osmotic pressure. The electrical properties of solutions are given **38** pages with emphasis upon the Arrhenius theory and the degree of ionization. Colloidal solutions are treated in 10 pages.

Part III, pp. 295–466, deals with the nature of reactions. The author first devotes a chapter to the speed of reactions. The equilibrium constant is then introduced as the quotient of two rate constants. The phase rule, equilibrium in gaseous reactions, the Ostwald dilutions law, with emphasis upon the concentration of the ions, valence equilibrium (oxidation, reduction and electromotive force), energy and free energy are treated in this section. The activity concept is given a third of a page.

Part IV, pp. 467–543, is an application of the foregoing principles to special ionic equilibria: solubility products, indicators, hydrolysis, complex ions.

An outline at the beginning of each chapter and many excellent exercises increase the usability of the book. Altogether the author has given us an interesting book, quite free from errors. The reviewer feels that this work will find favor as a text in a chemistry curriculum in which the ideas of Physical Chemistry are reserved to special courses. The theoretical chemistry which should be given college freshmen is reviewed, so that the book should be a valuable reference work for advanced students.

MERLE RANDALL

Organic Laboratory Methods. By the Late Professor LASSAR-COHN (Konigsberg). Authorized translation from the general part of the fifth revised edition. BY RALPH E. OESPER, PH.D., Associate Professor of Analytical Chemistry in the University of Cincinnati. Edited by ROGER ADAMS and HANS T. CLARKE. The Williams and Wilkins Company, Baltimore, Md., 1928. xi + 469 pp. 186 figs. 15.5 × 23.5 cm. Price, $6.50.

Lassar-Cohn's "Arbeitsmethoden für Organisch-Chemische Laboratorien" appears in the original German in two volumes, the first of which deals with laboratory technique, and the second with fundamental organic reactions such as nitration, etc. The present work is a translation of volume one. Its appearance is timely in that there are not many handbooks, written in English, which adequately cover this important subject.

There is a fairly broad diversity of topics, which include among others, distillation, dialysis, passage of vapors through hot tubes, evaporation, decolorization and clarification, extraction, filtration, crystallization, solvents and diluents, dehydration and comminution. It contains many useful suggestions, and should prove of especial value to graduate students majoring in organic chemistry. The stilted form which unfortunately characterizes so many translations is largely absent from this work. As a whole, then, it impresses the reader very favorably.

A. J. HILL

Gesammelte Abhandlungen zur Kenntnis der Kohle. (Assembled Scientific Papers on Coal.) Vol. 8, by DR. FRANZ FISCHER, Director of the Kaiser Wilhelm Institute for Research on Coal. Gebruder Borntraeger, Berlin, Germany, 1929. viii + 790 pp. Price, bound, $18.50.

This volume, like the preceding ones, consists of a collection of papers, for the most part previously published, dealing with the origin, constitution and utilization of coal. The papers included in the present volume give the results of researches carried out at the Institute during the years 1924 to 1927 inclusive. There are 111 in all, and of these 90 have appeared in *Brennstoff-Chemie,* 8 in various other periodicals and 13 are published here for the first time. A considerable proportion of the researches covered had for their objective the conversion of coal into oils, particularly by hydrogenation of carbonization products and by catalytic synthesis from water gas. The following titles will serve to illustrate the nature of this work: "The Reducibility of Cresols by the Bergius Method," "Petroleum Synthesis at Ordinary Pressures from the Gasification Products of Coal," "The Reduction and Hydrogenation of Carbon Monoxide," "Equilibrium Conditions in the Formation of Hydrocarbons and Alcohols from Water Gas." Bitumens extractable from coal and their relation to cokability are covered by several articles, and some experimental evidence is offered in support of the Fischer-Shrader lignin theory of the origin of coal. This book as well as the other seven volumes of the series will be found to be a valuable adjunct to libraries of those interested in coal research. They would be more readily usable if an index were provided.

JOSEPH D. DAVIS

Jahrbuch der Organischen Chemie. (Yearbook of Organic Chemistry.) BY Professor Dr. JULIUS SCHMIDT, Stuttgart. Franz Deuticke, Vienna, Austria, 1929. 17.5 × 25.5 cm. xviii + 256 pp. Price, unbound, M. 21; bound, M. 24.

The thirteenth volume of the Jahrbuch deals with investigations that were completed in 1926. For this tardy appearance which materially diminishes the value of such an annual, the author disclaims all responsibility, and he also gives assurance that, hereafter, the Jahrbuch will appear with its pre-war promptness and regularity. The general plan remains the same and there has been but little change in scope. The mechanical work of the new publisher is excellent.

E. P. KOHLER

The Theory of Emulsions and their Technical Treatment. By WILLIAM CLAYTON, D.Sc., F.I.C. Foreword by Professor F. G. Donnan, C.B.E., M.A., Ph.D., D.Sc., F.R.S. Second edition. P. Blakiston's Son and Company, 1012 Walnut St., Philadelphia, 1928. xi + 283 pp. 42 figs. 14 X 22.5 cm.

In writing the second edition the author has held to the same context as in the earlier book (160 pp., 1923). Theories of the formation of emulsions are discussed in great detail. A brief chapter on technical emulsions has been included.

Appendix I, written by W. Ramsden on the "Theory of emulsions stabilized by solid particles," might well have been elaborated as in the discussion on the important physical factor, "angle of contact," clarity appears to have been sacrificed for brevity.

Some condensation of the chapters on the theories of emulsions and elaboration of the chapters on de-emulsification and technical emulsions would probably have been welcomed by industry.

The comprehensive review of the literature presented by Clayton guarantees that a thorough knowledge of the subject may be obtained from this source. Mayonnaise is discussed with less than a page and no mention is made of the non-colloidal emulsifying agents. Yet many interesting ideas are included. Ayres' use of a solid fat, more readily wetted by oil than by water, as a water-in-oil emulsifying agent is worth noting. So is Schou's proposal to gelatinize soya bean oil at 250° and to mix it when cooled to 100° with twice its volume of cold soya bean oil in order to prepare an excellent water-in-oil emulsifying agent. The two-page list of emulsifying agents is especially useful.

Thirty-two pages of classified references are found in the Appendix.

The book contains much valuable information for workers in diverse fields. Biologists, pharmacists, chemical manufacturers and dairy chemists especially may profit.

HARRY N. HOLMES

Elektrizität und Eiweisse, insbesondere des Zellplasmas. (Electricity and Albumins, especially of the Cell Plasma.) By Dr. HANS PFEIFFER, Bremen. Theodor Steinkopff, Residenzstrasse **32,** Dresden-Blasewitz, Germany, 1929. xii + 149 pp. 7 figs. *15.5* X *22* cm. Price, unbound, R. M. 10; bound, R. M. 11.50.

This book is Volume XXI of a series, "Wissenschaftliche Forschungsberichte, naturwissenschaftliche Reihe," edited by R. E. Liesegang. The object of these monographs, as stated by the editor in an introductory note, is to offer in condensed form a selection of the most important accomplishments since about 1914, at home and abroad, in some single branch of natural science. This volume is concerned with a part of the field of electrophysiology, taking up (1) electrical properties of colloids, (2) electrical and colloidal properties of proteins, and **(3)** attempts to interpret the behavior of living cells from electrical measurements, and from the colloidal behavior of the cell proteins, It presents a very condensed abstract of the work of a large number of authors. (Over a thousand names are included in the author index.) It is evident that in so small a book the discussion of any one among so many papers must be extremely brief. Many of the references, indeed, are not mentioned in the text.

There is a subject as well as an author index. An improvement would be a list of the books and periodicals reviewed. An appendix gives a brief report of the symposium on Electrostatics in Biochemistry, at Basle, October 8–12, 1928.

EDWIN B. DAMON

Irving Langmuir
President of the American Chemical Society, 1929

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PRESIDENT'S ADDRESS[1]

MODERN CONCEPTS IN PHYSICS AND THEIR RELATION TO CHEMISTRY

BY IRVING LANGMUIR

Only about 35 years ago, during the nineties of the last century, knowledge of the physical sciences had advanced to such a point that many of the foremost physicists and chemists began to believe that the rate of progress of fundamental knowledge must be slowing up. The concepts of length, mass, time, energy, temperature, electric and gravitational fields, etc., had been given precise meanings and were regarded as having an absolute existence quite as certain as that of matter itself. The phenomena of nature were explainable in terms of natural laws expressing relations between these absolute quantities. It seemed that the most important of these laws of physics and chemistry had already been discovered and that the work that remained to do was largely a matter of filling in the details and applying these great principles for practical purposes.

The laws of mechanics had been verified experimentally with a high degree of precision so no one doubted that they were rigorous laws of nature. Back in about 1830, Hamilton had succeeded in generalizing these laws in a few simple equations which seemed to contain all the essential truths of mechanics. It was only necessary to know how the kinetic and potential energy of any given system varied with the momentum and the coordinates of its parts in order to have at least a formal solution of the way in which the system would behave at all times. Thus all future work in mechanics need only be considered an application of Hamilton's equations.

Complete knowledge of the nature of light presented more difficulties. Hamilton, about 1820, showed that all the known laws of geometrical optics could be explained quantitatively in terms of either a corpuscular theory of light or a wave theory. The experiments of Fresnel on the interference of light, which were made about this time, seemed to disprove Newton's

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[1] Presented before the 78th meeting of the American Chemical Society, Minneapolis, Minnesota, September 11, 1929.

corpuscular theory, so that Hamilton's proof of the complete analogy between waves and corpuscles in the case of geometrical optics became only of academic interest. Through the study of the phenomena of interference, diffraction, polarization and absorption of light, the wave theory of light became firmly established. Light was supposed to consist of waves in some sort of an elastic medium which was called the ether.

About 1830, Faraday developed clear conceptions regarding the electric and magnetic fields and Maxwell, about 1860, by applying exact mathematical methods evolved the electro-magnetic theory of light according to which light waves consisted of fluctuating electric and magnetic fields which are propagated through space at a speed which could be calculated from electric and from magnetic measurements in a laboratory.

Although the acceptance of Maxwell's views came slowly one could not long remain skeptical after the production of electro-magnetic waves of relatively great wave length by Hertz in 1884. It may almost be said that Maxwell's theory was essentially an application of the mathematical methods which Hamilton had originated in his treatment of the laws of mechanics, to Faraday's concepts of electricity and magnetism.

Thus in 1895, the physicists seemed to have some justification for the attitude that the most important laws had been discovered. The laws of mechanics had not been improved upon in 65 years. Faraday and Maxwell had brought in precise conceptions of electric and magnetic phenomena and had shown that by classical methods like those which had been so successful in mechanics, all the laws of optics could be derived from those of electro-magnetism.

In chemistry a somewhat similar state had been reached. After the evolution of the conception of the elements and of combining proportions based upon an atomic theory, rapid progress was made in accumulating data regarding the elements and their compounds. Faraday's laws of electrolysis and new methods for the accurate determination of atomic weights began to provide the chemist with quantitative laws almost as precise as those of the physicists. The work of J. Willard Gibbs had brought into chemistry rigorous laws as fundamental in their field of application as were those of Hamilton and Maxwell in physics.

These remarkable advances on the quantitative side seemed to overshadow in importance the more qualitative results that had previously been obtained through the stimulus of the atomic theory. Under the leadership of Ostwald, chemists began to adopt a much more critical attitude and began to distinguish carefully between what they considered experimental facts and hypotheses based upon these facts. Ostwald, although he recognized the convenience of the atomic theory, believed it must always remain impossible to prove the existence of atoms or molecules. He therefore urged that chemists avoid as far as possible the use of such hypotheses. Perhaps the chief result of this attitude was to lead physical chemists to neglect those parts of chemistry where the atomic theory would have been most helpful and to devote themselves more specially to the fields in which energy relationships and thermodynamics were directly applicable.

Physicists in general did not doubt the existence of atoms and molecules, but had by means of this theory developed the kinetic theory of gases which had led to many new quantitative laws, verified by experiment. However, the physicists in general had little to do with atoms and molecules but were more concerned with the ether, in which they believed unreservedly, although direct knowledge of the ether was far harder to obtain than knowledge of atoms and molecules.

Perhaps one of the main reasons why the physicists were so sure of the ether and the chemists so doubtful of the atoms and molecules was an unconscious belief in the respectable old adage "Natura non facit saltum," Nature makes no jumps. Certainly in those fields of physics and chemistry in which rigorous quantitative laws had been found applicable no discontinuities or jumps such as those implied by the atomic theory had been found.

The discovery of x-rays by Roentgen, in 1905, marked the beginning of an extraordinary revolution which is today still in progress. This sensational event revealed to the physicist that great and fundamental discoveries were still possible even in the field of radiation where physics had had such complete success. It immediately caused great numbers of physicists to study the phenomena of electric discharges and to look for other sources of radiation. The-discovery of radium and radioactivity by Becquerel and the Curies soon showed the importance of these new forms of radiation to the chemist as well as to the physicist.

Although Stoney in 1874 had seen that Faraday's laws of electrolysis together with the atomic theory required that electricity should also have an atomic structure, and although in 1891 he proposed the name electron for these atoms of electricity, J. J. Thomson should be regarded as the discoverer of the electron. He was able to show that electrons were contained in all forms of matter and found that the electron must weigh only about $^1/_{1800}$ as much as a hydrogen atom.

The studies of radioactivity, largely by Rutherford and his students, showed that radium spontaneously disintegrated to form helium and proved to the chemist that atoms were not indestructible and even that transmutation of elements was possible.

By the application of thermodynamics to radiation processes Boltzmann proved that the total radiation, of all wave lengths, within a cavity in a heated body must increase in proportion to the fourth power of the absolute temperature; this law had already been found empirically by Stefan. By a further development of thermodynamic methods Wien, in 1896, derived an important law, known as Wien's law, by which the intensity of radiation of any particular wave length could be calculated in terms of the wave length and temperature. This law was found to agree with experiment in the case of visible radiation from incandescent solids, but serious discrepancies were observed when an attempt was made to calculate the intensity of infra-red radiation or heat waves. Lord Rayleigh and Jeans, in 1900, using what seemed to be unimpeachable methods based on the electro-magnetic theory of light, arrived at an entirely different relation between the intensity of radiation and the temperature and wave length. This equation agreed excellently with experiments on the radiation of heat where Wien's law had failed but led to absurd results when applied to the shorter wave lengths of the visible spectrum. In fact, if the total radiation including all wave lengths were calculated from the Rayleigh-Jeans equations an infinite radiation density was obtained even at low temperatures. Thus by means of the classical theories of radiation it was found on the one hand by Boltzmann that the radiation increased with the fourth power of the temperature, and on the other by Rayleigh–Jeans, that the radiation was infinite at all temperatures.

It was shown in 1905, by Planck, that this paradox could only be solved by assuming an essential discontinuity in the energies or motions of electrons whose vibrations caused the radiation. This gave birth to the Quantum Theory, which within recent years has grown to be one of the most important theories of physics and chemistry. In 1906, Einstein showed that the photo-electric effect and many photochemical reactions could be explained in terms of the Quantum Theory if light itself consisted of discrete particles of energy or quanta, now usually called photons. Although such a corpuscular theory of light seemed utterly incompatible with the accepted wave theory, an increasing number of phenomena were discovered in which it seemed necessary to resort to this corpuscular theory. The really rapid development of the Quantum Theory, however, dates from 1913, when Bohr began to develop his theory of atomic structure by applying the Quantum Theory to Rutherford's more or less qualitative theory of the nuclear atom.

Relativity Theory.—Among all the changes in the ways of thinking which were being forced upon physicists at this time, the most important by far was that which resulted from Einstein's relativity theory, first stated in 1905. In 1895, as we have seen, electromagnetic waves and matter were thought to be manifestations of the properties of an all pervading ether.

As an example of the way that the physicists thought of the ether I will quote from the preface to Lord Kelvin's "Baltimore Lectures." This preface was written in 1904, but the lectures were those that were delivered at Johns Hopkins University in 1884.

"I chose as subject the 'Wave Theory of Light' with the intention of accentuating its failures; rather than of setting forth the admirable success with which this beautiful theory had explained all that was known of light before the time of Fresnel and Thomas Young, and had produced floods of new knowledge splendidly enriching the whole domain of physical science. My audience was to consist of Professorial fellow-students in physical science. . . . I spoke with absolute freedom and had never the slightest fear of undermining their perfect faith in ether and its light-giving waves: by anything I could tell them of the imperfection of our mathematics; of the insufficiencyor faultiness of our views regarding the dynamieal qualities of ether; and of the overwhelmingly great difficulty of finding a field of action for ether among the atoms of ponderable matter. We all felt the difficulties were to be faced and not to be evaded; were to be taken to heart *with the hope of solving them if possible.* . . . It is in some measure satisfactory to me and I hope it will be satisfactory to all my Baltimore coefficients still alive in our world of science, when this volume reaches their hands to find in it dynamical explanations of every one of the difficulties with which we were concerned from the first to the last of our twenty lectures of 1884. All of us will, I am sure, feel sympathetically interested in knowing that two of ourselves, Michelson and Morley, have by their great experimental work on the motion of ether relatively to the earth, raised the one and only serious objection against our dynamical explanations."

.This Michelson and Morley experiment of 1887, through the theoretical investigations of Lorentz and others, kept growing in importance until it finally stimulated Einstein to evolve his relativity theory.

According to this theory space and time cannot be considered as existing independently of each other. They cannot in any sense be regarded as absolute but are both dependent upon the point of view of the observer. For example, Einstein showed that it has no meaning to say that two events which took place at a great distance apart occurred simultaneously. Some observers knowing of both events would have to say that event A occurred before B, while other observers moving at a different velocity from the first observers would conclude that B occurred before A.

It is not my plan to try to explain the relativity theory to you even if I knew how to do so, but it is rather to discuss the way in which this theory and others of **a** somewhat similar nature have gradually brought about profound changes in the viewpoint of the physicists and how similar changes are beginning to occur in the attitude of the chemists. The importance of Einstein's work thus lies not so much in the facts or phenomena that can be explained by the relativity theory, but in the discovery of a new way of thinking as applied to physics. Somewhat similar methods of thought had, it is true, been used in some branches of mathematics and sometimes in philosophy, but Einstein subjected our elementary conceptions of space, time, mass, energy, etc., to a searching analysis quite new in the history of physics.

Concepts Involve Operations.—Professor P. W. Bridgman of Harvard University has recently written a popular book entitled "The Logic of Modern Physics," in which he analyzes the changes in our concepts that have resulted primarily from Einstein's work. Bridgman's thesis is that *physical concepts have meaning only in so far as they can be defined in terms of operations.* He shows that this new attitude toward our fundamental conceptions is perhaps one of the greatest changes that has been brought about by Einstein's work. There is no question in my mind but that the recent remarkable advances in quantum mechanics that have been made by such men as Bohr, Heisenberg, Schroedinger and Dirac have been stimulated by the desire to formulate all concepts in terms of operations. Bridgman has not originated this method, but he, more than anyone else, perhaps, has been conscious of its widespread application in modern physics.

I should like to outline to you the way in which Bridgman develops this thesis and to consider how well it applies to the most recent changes that have taken place in physics and in chemistry. I believe the chemist can derive great benefit from the conscious application of a similar critical attitude in his own science.

Bridgman points out that "hitherto many of the concepts of physics have been defined in terms of their properties." An excellent example is Newton's concept of absolute time. The following quotation from Newton's "Principia" is illuminating.

"I do not define Time, Space, Place or Motion, as being well known to all. Only I must observe that the vulgar conceive those quantities under no other notions but from the relation they bear to sensible objects. And thence arise certain prejudices, for the removing of which, it will be convenient to distinguish them into Absolute and Relative, True and Apparent, Mathematical and Common.

"(1) Absolute, True and Mathematical Time, of itself, and from its own nature flows equally without regard to anything external, and by another name is called Duration."

Thus, according to Newton, time and space have properties of a very abstract kind and are looked upon as "things" which exist independently of all other things. There is, however, as Bridgman says, "no assurance whatever that there exists in nature anything with properties like those assumed in the definition, and physics, when reduced to concepts of this character, becomes as purely an abstract science and as far removed from reality as the abstract geometry of the mathematicians." Nevertheless, these conceptions of space and time prevailed until the relativity theory was proposed.

In the development of his theory Einstein, in analyzing the concepts of space and time, considered what means are available by which an observer can measure distances between two points on a rapidly moving object. For example, imagine two planets moving past each other at high velocity and two observers, one on each planet, provided with means for observing each other and communicating with each other; such means, for example, as light signals. Einstein asks, what are the operations by which the two observers could compare their units of length and time? He finds that each observer would logically conclude that the other observer's unit of length is shorter than his own, and that the other's unit of time is longer than his own. Einstein thus proved that there can be no such thing as absolute length or time, or rather proved that the concept of absolute time has no meaning, for we have not been able to conceive of any method for determining the absolute time of any event.

In order to illustrate his thesis Bridgman considers in detail the concept of length. Probably one of the earliest concepts of length was obtained by counting the number of unit lengths that can be placed end to end between two given objects. For example, the number of paces are counted in walking from one object to another. An extension and refinement of this method is employed today when the standard meter at the Bureau of Standards is compared with a steel tape and this is then used to lay off a base line for a survey by triangulation.

As Bridgman suggests, it was one of the greatest discoveries of the human race to find that these operations performed with a measuring rod afford a useful and convenient means of describing natural phenomena.

During the transition from the earliest pacing of distances, to our modern refined measurements with the meter stick, the concept of length itself must have undergone radical modifications since the operations involved had been modified. For example, if distances are to be paced, it has no meaning to consider distances of $^1/_{1000}$ of a pace unless the concept is modified to include arbitrarily chosen methods by which a length equal to $^1/_{1000}$ of a pace may be determined. In our modern measurements with a steel tape we must measure the temperature of the tape and the force used in holding the tape taut, and then by means of the coefficient of expansion and the coefficient of elasticity, apply corrections to the observed length. It is hard to see what methods primitive man could have used in applying such corrections to his distances measured by pacing.

Why do we now apply such corrections? Merely because it has been found by experiment that the result that we get by applying such corrections is a quantity which proves to be more useful in describing natural phenomena than the results we get without these corrections. We must not think that we do it in order to obtain the "true" or "absolute" length.

Today we have many other methods of measuring length than by use of measuring rods or steel tape. For example, we use optical instruments and measure distances by triangulation, we measure heights in the atmosphere by means of a barometer, we measure the distances of spiral nebulae by measuring the brightness of the Cepheid variables observed in them by our most powerful telescopes, we measure the lengths of molecules by finding the area of a water surface over which a given amount of oil will spread, we calculate the diameters of molecules by measurements of the viscosity of gases by means of the kinetic theory, or we use x-ray diffraction patterns or, finally, we calculate the diameter of an electron from its mass and charge by means of the electro-magnetic theory assuming that all the energy of an electron lies in the electric field outside of its surface.

Now each of these measurements of length involves an entirely different set of operations and, therefore, fundamentally, according to Bridgman, we should regard them as different concepts; logically, in fact, they should all have different names. It has, however, been found as a matter of experiment that two or more of these methods when applied to the measurement of the same distance give results which agree more or less with one another. This, then, is our justification for calling all these concepts by the same name, length.

We may, if we wish, extrapolate and predict that by applying suitable corrections to each of these methods of measuring lengths we may be able to get better and better agreement between them. Such methods of extrapolation may be useful and stimulating but we must always expect that sooner or later we will be unable to obtain agreement between these methods with more than a limited degree of accuracy. This may not be due merely to experimental difficulties but may often result from unavoidable fuzziness in the concept itself. Such concepts as the diameter of a complicated molecule, or the mean free path of a molecule in a gas are inherently fuzzy conceptions and can mean not much more than when we speak of the diameter of a tree or of the length of the waves during a storm at sea.

Perhaps the strongest reason for the general belief in the existence of an absolute space lay in the apparently perfect agreement between our measurements of length and the theorems of Euclidian Geometry. During the last century, however, mathematicians began more and more to realize that Euclidian Geometry was only one out of many possible logical geometries, and since all of these were based solely on certain axioms or postulates none of them had any real or necessary connection with physics. The apparent agreement between our physical observations and Euclidian Geometry, therefore, does not prove that space must have the properties postulated in Euclid's axioms.

Models.—As chemists we are all more or less familiar with various models of atoms and molecules that have been proposed within recent years. The structural formulas which the organic chemists have used for a good part of a century are another example of an extremely useful type of model. I want to discuss later some of the models which the physicists have used in giving more concrete forms to their theories. Logically, I believe, we should regard Euclidian Geometry as a model devised primarily to help us "explain" natural phenomena.

Observation of nature reveals great complexity. We receive enormous numbers of impressions simultaneously and if we are to make progress in understanding phenomena we must concentrate on certain aspects of the things we see about us and thus discard the less important features. This involves a process of replacing the natural world by a set of abstractions which we have become very skilful in choosing in such a way as to aid us in classifying and understanding phenomena. Thus it was found useful to develop concepts or abstractions such as shape, position, distance, etc., and separate these characteristics of the phenomena from others such as color, hardness, etc. Euclidian Geometry was found useful in correlating these concepts of shape, position, etc.

Physicists and chemists have usually felt that they understood a phenomenon best when they could explain it in terms of a model or concrete picture. The chemist explained the law of multiple combining proportions in terms of atoms which combine together to form molecules. The heat conductivity, viscosity, etc., of gases was explained in terms of the kinetic theory, with molecules making elastic collisions with one another according to the law of probability.

When we use the atomic or molecular theories to explain phenomena in this way, we assign to the atoms and molecules only those properties which seem needed to accomplish the desired result, we do not consider what the atom is made of nor what its structure is, but usually feel justified in assuming properties which are as simple as possible. For example, in the elementary kinetic theory it is assumed that the molecules are hard, elastic spheres, not because anyone really believes that molecules have these properties, but merely because these are the simplest properties we can think of which are consistent with the known facts.

What we really do, therefore, is to replace in our minds the actual gases which we observe and which have many properties which we do not fully understand by a simplified model, a human abstraction, which is so designed by us that it has some of the properties of the thing we wish to displace.

There is thus a difference of degree rather than of kind between the adoption of a mechanical model and the development of a mathematical theory such as Euclidian Geometry. When the mathematical physicist develops an abstract theory of actual phenomena, for example, Hamilton's equations to summarize the laws of mechanics, he is in reality constructing a mathematical model. Mathematical equations have certain definite properties or rather they express certain relationships between the symbols which enter them. In a mathematical theory of physical phenomena the equations are so chosen that the relation between the symbols corresponds in some simple way to that which is observed between measurable physical quantities which are the bases of our concepts of physics.

Within recent years, especially in the development of the relativity and quantum theories, physicists have been making increasing use of mathematical forms of expression, and have been giving less attention to the development of mechanical models. The older generation of physicists and chemists and those among the younger men who are less skilled in the use of mathematics are inclined to believe that this is only a temporary stage and that ultimately we must be able to form a concrete picture or model of the atom, that is, to get a picture of what the atom is really like. It seems to be felt that a mechanical model whose functioning can be understood without the aid of mathematics, even if it only gives the qualitative representation of the phenomena in question, can represent the truth in some higher sense than a mathematical theory whose symbols perhaps can be understood only by a mathematician.

There is, I believe, no adequate justification for this attitude. Mechanical models are necessarily very much restricted in scope. The relationships of their parts are limited to those that are already known in mechanics (or in electricity or magnetism). Mathematical relationships are far more flexible; practically any conceivable quantitative or qualitative relationship can be expressed if desired in mathematical form. We have no guarantee whatever that nature is so constructed that it can be adequately described in terms of mechanical or electrical models; it is much more probable that our most fundamental relationships can only be expressed mathematically, if at all.

In analyzing our attempts to describe nature, we have discussed concepts, models and mathematical theories. We find that they are all alike in that they represent human abstractions which are found convenient in describing nature. Going back a step further we must recognize that *words* themselves constitute elementary concepts. They are, it is true, much more vaguely defined than our concepts of physics and chemistry, but qualitatively they are very much like the latter; in fact, most of our misunderstandings in science arise from assigning reality to concepts whose main reason for existence is the fact that they are represented by a word. Logically we should aim to define our words in terms of operations. We should have in mind specifications by which we can test whether or not the word is properly applicable.

The progress of science depends largely upon (1) giving to words meanings as precise as possible; (2) definition of concepts in terms of operations; (3) development of models (mechanical or mathematical) which have properties analogous to those of phenomena which we have observed.

Meaningless Questions.—A great deal of time and effort is wasted in scientific circles as well as in the world at large through failure to give sufficiently definite or useful definition of words and concepts. Bridgman emphasizes this in connection with his discussion of "Meaningless Questions."

In some cases questions fail to have meaning because of the more or less inherent fuzziness of the concepts involved. For example, if we compare two trees of about the same size it may have no meaning to ask which tree has the larger diameter, for no one has defined the diameter of a tree with the necessary precision.

A more important class of meaningless questions arises when there are no conceivable operations that could be performed to arrive at a decision. For example, what is the meaning of the question, "Would the United States have ended the World War if the Lusitania had not been sunk?" Such a question may be a good subject for a school debating society, but no one is apt to think that the question has thereby been answered.

A study of meaningless questions may serve a very useful purpose in science. A statement that a certain question has no meaning may be equivalent to stating a fundamental law of nature; for example, to say that the question "What is the true velocity of the north star through space?" has no meaning is a fairly good statement of at least a part of the relativity theory.

In some cases it may have no meaning to ask whether or not there is a magnetic field in a certain portion of space. For example, suppose an observer, stationary on the earth, studies an electron in motion. The motion of an electron constitutes an electric current and experimentally he will observe the characteristic magnetic field surrounding this electron corresponding to this current. If another observer moves along with the electron, it will appear to him to be at rest, and, of course, he can observe no magnetic field. Otherwise, the presence or absence of a magnetic field around an electron or group of electrons could be used to determine absolute motion through space, which would be contrary to the relativity theory. The relativity theory thus requires that a magnetic field can have no real existence in any absolute sense.

We have seen that there are fundamentally as many different concepts of length as there are different ways in which length may be measured; nevertheless, we find approximate agreement between different ways of measuring the diameter of molecules and therefore are justified in assigning some *reality* to the concept diameter of molecule. When, however, we ask what is the diameter of an electron, we find that the question is practically without meaning. It is true that we can calculate, a diameter by assuming that the electron behaves like a charged sphere and that the classical laws of electrodynamics can be applied in this case. However, since we have no independent way of measuring this diameter, the process is one which involves reasoning in a circle.

There are many meaningless questions which afflict the chemist. It clearly has no meaning to ask what is the molecular weight of sodium chloride in a crystal. It is very doubtful whether it has any meaning to ask what is the molecular weight of water in liquid water. There are many cases where the concept of temperature has no definite meaning. Strictly speaking, temperature acquires meaning in terms of operations only in so far as an approach is made to equilibrium conditions. When the motions of molecules or atoms follow Maxwell's Distribution Law, that is, a random or probability distribution of velocity among the molecules, the concept of temperature becomes very definite. If, however, we deal with mercury vapor streaming into a high vacuum, or the conditions near a hot tungsten filament in a gas of low pressure, temperature has very little meaning. The same is true of the conditions frequently existing in an electric discharge tube such as a mercury arc, where the electrons act as though they had a temperature of perhaps 50,000°, whereas the atoms have motions corresponding to far lower temperatures. Strictly speaking, neither the electrons nor atoms have well-defined temperatures, for the conditions are far removed from equilibrium.

In much of the recent discussion of the Radiation Hypothesis of chemical reactions, chemists have been discussing meaningless questions usually without realizing it. At first it was proposed that the radiation is absorbed by the reacting gas to form excited molecules in accordance with Einstein's photochemical law. When this is found not to be in accord with experiment, the concept of radiation is altered repeatedly as new experimental facts are found so as to make the modified theory continue to fit the facts. After this process has been carried on sufficiently, it no longer has any meaning to ask whether the reaction is caused.by radiation or whether the radiation hypothesis is true.

In the studies of the properties of liquids, questions of the degree of ionization and of association and in some cases of internal pressures have been discussions of questions without meaning. A great deal of such discussion might be simplified or even avoided entirely if chemists would agree in defining these concepts in terms of operations.

Theories of valence within recent years have been afflicted with 'the same difficulties. As long as chemists deal with the ordinary valence rules of organic chemistry, they are dealing with concepts of valence which are actually defined in terms of operations; that is, the organic chemists know how to conduct experiments to prove that the valence of nitrogen in dimethylaniline is 3. The types of operations needed to establish the valence of magaesium in magnesium chloride are in many ways quite different, and they are still different if we consider the case of so-called quinquevalent nitrogen in ammonium chloride or heptavalent chlorine in perchloric acid. I believe that the chemist has much to learn from the physicist in regard to the proper method of attacking. such problems as these.

The electrochemist has been troubled in locating the source of electromotive force in cells. The physicist has similar difficulty in finding the origin of the contact potential between metals. Fundamentally it must be recognized that unless or until there are methods by which these quantities can be measured, questions involving them have no meaning.

A practical example of the meaninglessness of some questions involving electric potential has recently arisen in the numerous proposals that have been made to construct a speed indicator for airplanes which will give the speed with respect to the earth's surface independently of that of the wind surrounding the plane. It is reasoned that since the plane is moving through the earth's magnetic field a potential will be set up between the ends of a wire stretched between the wing's tips. It is only necessary to measure this potential difference in order to calculate the speed of the plane with respect to the earth. Careful analysis shows that the concept of the potential difference under these conditions is meaningless except with reference to a particular reference system. If this system is referred to the plane itself, this potential difference is zero quite regardless of what the speed of the plane may be with reference to the earth. A contrary result would conflict with the relativity theory.

Meaningless questions will assume far greater importance in future years. We shall see that the latest forms of the quantum theory now give us the best of reasons for believing that the identity of separate electrons within atoms or molecules may be partly or wholly lost, so that it may have no meaning to ask whether a particular electron we find as a result of experiment is the same electron which has previously produced an observed phenomenon. Even more far-reaching in its consequences is the Bohr-Heisenberg Uncertainty Principle according to which it has no meaning to ask what is the precise position and velocity of an electron or atom. An electron may have a definite position or a definite velocity but it cannot in any exact sense have both. This doesn't mean merely that there are experimental difficulties in measuring them, it means that the concepts themselves (position and velocity) are relative to one another in a sense somewhat analogous to that of time and space in the relativity theory.

One's instinctive reaction when first questioned as to the objective reality of space, time, position, velocity, etc., is to object to such consideration on the grounds that they are too metaphysical. The recent advances in physics demonstrate that these methods of thinking are eminently practical; they represent, in fact, an attempt to get away from the metaphysical character of much of our thinking in the past. Instead of taking for granted objective realities corresponding to our concepts, we now deal with things which can be measured in the laboratory, the concrete data that we have to start from.

It is, however, very useful to retain the concept of reality. Bridgman suggests that reality should be measured by the number and the accuracy of the independent ways in which we arrive at similar measures of the concept in question. For example, owing to the fact that we have so many concordant methods of measuring the distance between the ends of a base line used for triangulation, we attribute great reality to the concept of length or, rather, to those concepts of length which are applicable in cases of this kind. We thus have some justification in saying that two points are really one kilometer apart. We do not attribute, however, much reality to the concept of the diameter of an electron.

Thirty years ago the physical chemist doubted the existence of atoms or believed the concept was useless if not pernicious. A few years later the leader of this movement, Ostwald, in the preface of one of his books stated that he believed that the existence of atoms had been proved experimentally beyond question, although in previous books he had stated that there are always an infinite number of hypotheses that could be advanced to explain any given set of experimental facts.

Today, what can we say in answer to the question "Does matter really consist of atoms?" Must we say that this is one of those meaningless questions?

Of course, the amount of meaning that can be attached to any such question depends upon the definitions of the words and concepts which it contains. If we mean by atoms indivisible and indestructible infinitely hard, elastic spheres, we are compelled to answer the question in the negative. In accordance with modern usage, however, we do not attribute any such properties to the atom. If, by the use of the word atom, we mean to imply principally the concept that matter consists of discrete particles which can be counted by the various methods which are now known for this purpose, we have the very best of reasons for answering the question in the affirmative. If in om studies of nature we discover evidences of discontinuities or of the presence of discrete natural units which can be correlated in a definite way with the numerical integers, we have come, it would seem, about as close to something absolute in nature as we can hope to get. Einstein in the relativity theory has taught us to look upon the intersections of world lines as the data upon which our observations of nature rest. Such points of intersections, which can be called events, are essentially discontinuities. In general they are all unlike one another. When we find in nature discrete units which in many respects appear to be identical with one another, and we can count these units, it would seem that the number of these units which obtain as a result is apt to be independent of our system of reference; therefore, they have in general, a certain kind of absolute significance.

In this respect, therefore, it seems that the atomic theory and the quantum theory in which integers play such a fundamental role may be considered as representing reality to a higher degree than almost any other of our physical and chemical theories.

Skepticism in regard to an absolute meaning of words, concepts, models or mathematical theories should not prevent us from using all these abstractions in describing natural phenomena. The progress of physical chemistry was probably set back many years by the failure of the chemists to take full advantage of the atomic theory in describing the phenomena that they observed. The rejection of the atomic theory for this purpose was, I believe, based primarily upon a mistaken attempt to describe nature in some absolute manner. That is, it was thought that such concepts as energy, entropy, temperature, chemical potential, etc., represented something far more nearly absolute in character than the concept of atoms and molecules, so that nature should preferably be described in terms of the former rather than the latter. We must now recognize, however, that all of these concepts are human inventions and have no absolute independent existence in nature. Our choice, therefore, cannot lie between fact and hypothesis, but only between two concepts (or between two models) which enable us to give a better or worse description of natural phenomena. By better or worse we mean, approximately, simpler or more complicated, more or less convenient, more or less general. If we compare Ostwald's attempts to teach chemistry without the use of the atomic theory with a good modern course based upon the atomic theory, we get an understanding of what should be meant by better or worse.

The more recent advances in atomic theory which have resulted from the development of the quantum theory and which have given us our present knowledge of atomic structure, afford us interesting applications of the new methods of thought, first introduced into physics and chemistry by the relativity theory.

The older atomic and molecular theories of the chemists took on more definite form through the development of the kinetic theory of gases, and through the electron theory and the study of radioactivity developed to a point where the atom is conceived of as consisting of a definite number of electrons revolving around the nucleus. The atom ceased to be indestructible and was no longer the smallest particle of matter which could take part in a chemical reaction. The nucleus, rather than the atom, became characteristic of the chemical elements. The chemical properties of the atom, however, depended upon the number and arrangement of electrons.

Bohr, in 1913, developed a marvellous new theory of the atom by combining Planck's quantum theory with a relative theory of the nuclear atom. He evolved several new quantitative mathematical relationships with new concepts such as energy levels, quantum states, etc., and showed how the spectra of elements could be explained in terms of these new concepts. He also gave a mechanical model consisting of electrons revolving in orbits about the nucleus according to laws which were partly classical and partly inconsistent with classical laws. This model enabled him to derive certain mathematical equations from which he was able to calculate the frequencies corresponding to the different lines in the spectra of hydrogen and other elements, these frequencies being obtained from fundamental quantities such as the charge and mass of the electron and the quantum constant h, and did not involve any quantities dependent on the properties of the elements in question. The agreement between the theory and experiment was practically perfect, often enabling the frequency to be calculated with an accuracy of one part in two hundred thousand.

Such remarkable success made most physicists and chemists believe that Bohr's model, for the hydrogen atom at least, was substantially correct. That is, they believed that Bohr's work proved that in a normal hydrogen atom the electron really described a circular orbit around a nucleus having a diameter and a frequency given by Bohr's model. Bohr himself never attached any such importance to the mechanical model, realizing that the important steps that he had taken consisted mainly in the introduction of new concepts and more particularly in the mathematical equations by which the observed frequencies in the spectral lines could be calculated.

Within recent years, largely through the work of Bohr himself and his students, and Sommerfeld, Schroedinger, and others, this theory of the hydrogen atom has undergone changes. According to Bohr's original model the radiation of energy corresponding to a spectral line resulted from transition in which the electron passed from one stationary orbit to another. No physical picture of this transition seemed possible. To account for the known phenomena it seemed necessary that the transition should occur so rapidly that the electron would have to move from one orbit to another with a velocity greater than that of light, and yet the train of waves in the resulting radiation lasted for relatively long periods of time, about 10^{-8} seconds. Radiant energy could be absorbed by the atom only if the frequency was just that which was capable of transferring an electron from one orbit to another definite orbit. Thus only one frequency could be absorbed at a time by an atom. It was found, however, that the frequencies corresponding to many lines could be scattered by a single atom. This seemed to require the presence within any given atom of a number of oscillators as great as the number of lines in the spectrum. One of the greatest arguments in favor of the original Bohr theory was that it avoided just this sort of complication in the atom.

To get rid of difficulties such as these, Heisenberg and Born realized that it was necessary to sweep out of the theories of atomic structure the many concepts which were characteristic of the mechanical models that had been proposed and to develop a mathematical theory of the atom which would involve only concepts that were definable in terms of operations. That is, the theory was one that dealt more directly with measurable quantities such as the frequencies of spectral lines. New methods of matrix calculus had to be evolved, a kind of calculus of discontinuities or discrete quantities instead of the calculus of continuous quantities which had characterized classical mechanics.

Only a little later Schroedinger, by developing DeBroglie's wave theory of quantum phenomena, was able to build up a theory that we will now refer to as the wave mechanics, according to which the whole atom with all its electrons can be looked upon as a wave phenomenon. The electrons are no longer considered to be moving in orbits. For example, the hydrogen atom is found to have spherical symmetry instead of the axial symmetry of the old Bohr model of the atom. Yet this theory leads to identically the same equations for the frequencies of the lines in the hydrogen spectrum. We must not say that Bohr's theory of the hydrogen atom has been overthrown. Bohr's *mechanical* model has been superseded, but the more important model which is represented by the equations and the concepts which he evolved is even better today than it was when it was first proposed.

. The wave mechanics which involves the calculus of continuous variables is not now in conflict with the Born matrix calculus of discrete quantities. The two theories are essentially merely different mathematical methods applied to a single fundamental problem. The resulting mathematical equations always agree with one another. One begins to believe that the mathematical theory is a far better model of the atom than any of the mechanical models which are possible.

The long-standing conflict between the wave theory of light and the corpuscular quantum theory now disappears with the new wave mechanics, the two aspects of light being somewhat analogous to the two aspects of the quantum theory, the wave mechanics and the matrix mechanics. In fact, the quantum theory now indicates that the electron itself can be regarded as a particle, or as a wave, just as light can be thought of as a photon or a wave. Whatever remained of the conflict between the wave and corpuscular theory of light and of the electron seems now to be fundamentally removed by the Bohr-Heisenberg Uncertainty Principle. To ask whether an electron is a particle or a wave is a meaningless question; the same is true of the question whether light consists of corpuscles or waves. One must answer that both of these are particles or waves according to the kind of operations that we may perform in observing them. If we make an experiment which proves that an electron has a very definite position, then it would seem to prove that it is a particle. In that case, however, according to the Uncertainty Principle, we are not able to determine accurately the velocity and therefore cannot predict where the particle will go.

Bohr has emphasized that the essential reason that the classical theory falls down in any detailed description of atomic phenomena is that our knowledge of such atomic systems can only be obtained through an act of observation which makes the observer inherently a part of the system. On the classical theory we assume that we could have knowledge of a completely closed system as though it were possible to know anything of what would go on in a strictly closed system. In order to make an observation some signal must be transmitted from the system to ourselves, and if we take this interaction completely into account we are forced to the quantum theory with its Uncertainty Principle.

An interesting feature of this new quantum mechanics is that the original conception of the relation between cause and effect which was universally accepted in science has lost its meaning. Atomic processes seem to be governed fundamentally by the law of probability. It has no meaning to ask when a particular radium atom will disintegrate, for no operation is conceivable by which such an event could be predicted. The same is true of every individual quantum process. We have no guarantee whatever that the expulsion of an a-particle from an atom of radium has any immediate cause. In chemistry the formation of nuclei in supercooled liquids, etc., must be essentially quantum phenomena in which no cause can be assigned for the formation of the individual nucleus. By varying the conditions we may alter the probability that a nucleus will appear at a given point, but in no absolute sense can we ever make a nucleus form through a direct cause.

By a deeper analysis of this question of causality Bohr concludes that we have an option of two alternative descriptions of natural phenomena. If we choose to describe phenomena in terms of ordinary space and time then we must abandon causality. We may, however, retain the conception of causality if we are willing to describe atomic phenomena in terms of what the mathematician calls configuration space. Consider, for example, a helium atom with its two electrons. If we attempt to give the position of both of these electrons in space we would need a set of three coördinates, x, y, z, for each of the electrons, that is, six coördinates in all, three of which belong to one and three to the other electron. The mathematician, however, finds that the two electrons in general could also be described by one point in six-dimensional space, for such a point **has** six coordinates. This is a representation of two electrons as a single point in a configuration space of six dimensions. Now it turns out from Schroedinger's theory that the motion of electrons, or rather of the waves corresponding to them, can be completely described in the case of the helium atom by a quantity which has a particular value at each point in this six-dimensional space or configuration space. The helium atom, however, can be described in terms of the motion of two electrons in three-dimensional space if we are content merely to know the probabilities that the electrons may be found at any point in this space.

These matters undoubtedly seem very abstract to those of you who have not previously become familar with them. I give them here mainly in order to illustrate how far the modern concepts of physics differ from those of twenty years ago.

If we must thus abandon our ordinary ideas of cause and effect, it may be asked why have the physicist and chemist so long believed that the whole teaching of science gave proof that every phenomenon resulted inevitably from the causes that led to it. I think the answer is that in the past scientists chose as the subjects for their investigations almost wholly those phenomena in which such definite relations as cause and effect could be found. These phenomena are those in which such enormous numbers of individual quantum phenomena are grouped together that the result is determined only by their averages. For example, when we study the variation of the pressure with the volume of a gas, the forces that we measure result from the impacts of great numbers of molecules, the average force remaining steady and definite. If, however, we only had one molecule in a small volume, the pressure exerted on the walls would be zero except for those instants at which the molecules struck the wall. It would then be impossible to predict in advance what the pressure would be at a particular time.

I think in trying to estimate the reliability of any of our scientific knowledge we should keep in mind that the whole complexion of a science may be made to change by the psychology of the investigators which governs the choice of the subjects that are investigated.

Our best knowledge of time and its relation to other concepts is that which we have obtained through Einstein. Yet in the whole relativity theory there is nothing to distinguish between positive and negative time, that is, between future and past, any more than there is between different directions in space, such as right and left. There thus appears to be something curiously incomplete in our knowledge of time, for every one of us knows the vast practical diierence between past and future. Eddington, in his recent book, "The Nature of the Physical World," discusses the "arrow of time" at some length. He suggests that the second law of thermodynamics is the only fundamental law of nature which provides us with any distinction between future and past. One way of stating this law is that all spontaneous processes that occur in nature involve an increase in entropy. Eddington thus proposes that the positive direction of time can be defined as that direction in which the entropy increases. If we had a system in absolute equilibrium the entropy would be constant, and there would then be no arrow of time. This is in accord with the fact that in such a system there are no changes with time.

It is improbable that there are two independent fundamental factors which provide an arrow for time, so that it would seem that Eddington in having found one such factor has found the only one. There are, however, grave difficulties with this view. An arrow is a vector quantity which should have magnitude as well as direction. Now the rate of change of entropy does not seem to give us any measure of time. For this purpose we use phenomena which are as nearly reversible as possible, such as the swinging of a pendulum in a vacuum.

Fundamentally entropy is a measure of randomness. A random distribution of molecules in space and velocity is a system having the maximum entropy. If we throw a pack of cards out of the window and collect them from the ground they have become effectively shuffled. We would not expect by this process, starting with a shuffled pack of cards, to find them at the end in the order in which they come from the manufacturer. The direction in which the randomness increases thus provides an arrow for time. This arrow is, however, equivalent to that involving the increase of entropy.

It is still an open question, however, whether processes directed by intelligent beings may not involve a decrease in entropy. In fact it seems conceivable that the evolution of organic life on the earth is in some measure fundamentally contrary to the second law of thermodynamics. The inherent tendency of evolution seems to be to bring about an ordered rather than a random arrangement of parts, and in the future perhaps forms of life may evolve which cause a decrease of entropy on a large scale. Are we then to have some parts of the universe in which the arrow of time points in the opposite direction from that in neighboring parts?

Such speculations may seem fantastic, It is, however, I believe, of the utmost importance for the chemists and the physicists to evolve fundamentally sound conceptions of such things as time and entropy.

The profound changes in physical thought, particularly those represented by the Quantum Theory, are rapidly bringing about a revolution in physical chemistry. The third law of thermodynamics involving chemical constants has changed radically our methods of studying chemical equilibria. The application of the Quantum Theory to band spectra promises to be of the utmost importance in chemistry. By enabling us to determine the moments of inertia of chemical molecules, the actual distances between the nuclei of the atoms in molecules can be found. Apparently our most accurate determinations of the heats of dissociation of elementary gases can be obtained from the band spectra through a knowledge of the energy levels of the various possible states of the molecules. In recent numbers of the "Journal of the American Chemical Society," particularly in the paper of Giauque and Johnston, we see the beginnings of what promises to be the most accurate and fertile source of knowledge of chemical equilibria. From a detailed knowledge of the spectrum, for example, of oxygen, and without recourse to any other experimental determinations, the specific heat at all temperatures can be calculated, and the entropy of oxygen at all temperatures is thus found. This, together with the heats of reactions, which may be found by a similar method, makes possible the calculation of the degree of dissociation of oxygen and will ultimately make possible the calculation of all chemical equilibria.

The remarkable work of Dennison, Bonhoeffer and Eucken in predicting and isolating para-hydrogen should prove to the chemist how many of his chemical discoveries will be obtained in the future by the application of these new theories of physics.

Gurney and Condon have recently derived from the wave mechanics an explanation of the fundamental law of radioactivity. Similar methods will probably before long enable us to understand the processes involved in chemical reactions far better than we ever have before.

Physics and chemistry are being inevitably drawn closer together. It seems that there has never been a time when we can predict with such certainty rapid progress in fundamental chemistry, for the new theories of physics have as yet scarcely begun to be applied in the field of chemistry. The physicist on the other hand has much to learn from an increased knowledge of chemical phenomena which should provide him with a richness of experimental data far greater than any he has yet had an opportunity to use.

Unfortunately, although theoretical physics and chemistry are thus supplementing each other and in many respects are being merged into a new science, there are remarkably few men as yet that have received adequate training in both sciences. Before long, I hope, sharp distinctions between physics and chemistry will no longer exist, but at present there seems to be a very practical distinction.

In order to find approximately how many chemists are also active as physicists and *vice versa,* I have selected at random 100 pages of the fourth edition of American Men of Science (1927) which contains the names of 13,500 American scientists. Of these, approximately 2700 are classed as chemists and 760 as physicists. Of the chemists 87% are members of the American Chemical Society, while only 2.5% belong also to the American Physical Society. Seventy-seven per cent. of the physicists are members of the American Physical Society, while 3.3% are also members of the American Chemical Society. Thus only about 3% of the physicists and chemists of the United States, whose names are given in the American Men of Science, belong to both of the national societies. This leaves far too small a number of men who are capable or are properly prepared to carry on the important work of bringing these two sciences closer together.

To pave the way for the coming revolutionary changes in chemistry we must be prepared to modify our methods of thinking, probably along lines now so prevalent in physics. But above all we must urge young chemists in the universities and after graduation to become thoroughly well trained in mathematics and in modem physics.

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THE MOLECULAR STRUCTURE OF THE TUNGSTOSILICATES AND RELATED COMPOUNDS

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1. Introduction

The molecular structure of the heteropolyacids[1] such as 12-tungstosilicic acid, $H_4SiW_{12}O_{40}\cdot xH_2O$, has long been the subject of speculation. A structure based upon Werner's coordination theory, suggested by Miolati,[2] has been developed and extensively applied in the systematization of heteropolyacids by Rosenheim,[3] and now is generally used in the discussion of these acids.[4] The Miolati-Rosenheim conception is, however, far from satisfactory. It provides no explanation for the characteristic properties of these acids and their salts, and the single definite pre-

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[1] A historical summary of work on the heteropolyacids, with complete references to the papers of C. Marignac, F. Kehrmann, H. Copaux, W. Gibbs and many other investigators, is given by A. Rosenheim and J. Jaenicke, *Z. anorg. Chem.*, 100,304 (1917).

[2] A. Miolati, *J. prakt. Chem.*, [2] 77, 417 (1908).

[3] (a) A. Rosenheim and co-workers, *Z. anorg. Chem.*, 69, 247 (1910); (b) 69, 261 (1910); (c) 70, 73 (1911); (d) 70, 418 (1911); (e) 75, 141 (1912); (f) 77, 239 (1912); (g) 79, 292 (1913); (h) 84, 217 (1913); (i) 89, 224 (1914); (j) 91, 75 (1915); (k) 93, 273 (1915); (l) 96, 139 (1916); (m) 100, 304 (1917); (n) 101,215 (1917); (o) 101,235 (1917).

[4] F. Ephraim, "Inorganic Chemistry," Gurney and Jackson, London, 1926, pp. 405–419; J. N. Friend, "A Textbook of Inorganic Chemistry," Griffin, London, 1926, Vol. VII, Part III, pp. 251–268; etc.

diction which it makes, concerning the number of acid hydrogen atoms, is in disagreement with the results of experiment.

By applying the principles which have been found to underlie the formation of coordinated structures in crystals, I have deduced a structure which accounts for all of the characteristic properties of the heteropolyacids; namely (1) the existence of a series of stable and eminently crystallizable compounds such as $H_4SiW_{12}O_{40}\cdot 31H_2O$ differing greatly in properties from the acids H_2WO_4, $H_2W_2O_7$, etc.; (2) the number of replaceable hydrogen atoms in these acids; (3) the number of molecules of water of crystallization in crystals of the acids and their salts; (4) the crystal form of the acids and their salts; and (5) the tendency of the 12-acids to condense to similar acids, such as $H_3PW_9O_{31}\cdot xH_2O$, in which the number of tungsten or molybdenum atoms per central atom is less than twelve; and which further leads to a number of predictions regarding the attributes of these substances which can be tested by means of the experiments that they suggest.

2. The Classification of the Molybdenum and Tungsten Polyacids. **The** Miolati-Rosenheim Theory

It was pointed out by Rosenheim[6] that there are two classes of heteropolyacids of molybdenum and tungsten, differentiated by their physical and chemical properties. Examples of the so-called 12-class are $H_4SiW_{12}O_{40}\cdot xH_2O$, $H_3PW_{12}O_{40}\cdot xH_2O$, etc.; of the 6-class $H_5I(MoO_4)_6$, etc. These acids, with 12 or 6 tungsten or molybdenum atoms per central atom, are called saturated 12-acids or 6-acids. Other members of each class exist in which the number of tungsten or molybdenum atoms per central atom is less than 12 or 6, respectively, but no well authenticated compound exists in which this ratio is greater than that for the saturated acids.

Copaux[6] prepared and analyzed a number of borotungstates, and observed the existence of isomorphism between borotungstates, silicotungstates, phosphotungstates and metatungstates, in the following cases

$5BaO\cdot B_2O_3\cdot 24WO_3\cdot 54H_2O$ $6BaO\cdot 2H_2O\cdot 24WO_3\cdot 53$ or $54H_2O$[7]	Orthorhombic, pseudocubic
$4H_2O\cdot 24WO_3\cdot 53H_2O$ $2H_2O\cdot 2SiO_2\cdot 24WO_3\cdot 50H_2O$ $3H_2O\cdot P_2O_5\cdot 24WO_3\cdot 48H_2O$	Trigonal, pseudocubic
$6K_2O\cdot 2H_2O\cdot 24WO_3\cdot 37H_2O$ $5K_2O\cdot B_2O_3\cdot 24WO_3\cdot 36H_2O$ $4K_2O\cdot 2SiO_2\cdot 24WO_3\cdot 36H_2O$	Hexagonal
$6(NH_4)_2O\cdot 2H_2O\cdot 24WO_3\cdot 46H_2O$ $5(NH_4)_2O\cdot B_2O_3\cdot 24WO_3\cdot 52H_2O$ $5H_2O\cdot B_2O_3\cdot 24WO_3\cdot 61H_2O$	Tetragonal, pseudocubic

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[5] A. Rosenheim, *Z. anorg. Chem.*, *96*, 139 (1916).

[6] H. Copaux, Ann. *chim. phys.*, [8] *17*, 217 (1909).

[7] See H. Copaux, *Z. anorg. Chem.*, *74*, 351 (1912). The exact water content of some of these substances is doubtful.

In addition he formed a series of solid solutions between potassium metatungstate and potassium silicotungstate. As a result of these observations he concluded that the metatungstates are to be considered as 12-tungstoacids in which water plays the role of the central group.

Rosenheim and Felix[8] similarly classified the tetra- and octomolybdates as 12-molybdates.

Salts representative of the 12-class and 6-class are tabulated below.

12-class		6-class	
$K_6H_2W_{12}O_{40}\cdot 18\frac{1}{2}H_2O$	$K_3PW_9O_{31}\cdot 7H_2O$	$K_5I(MoO_4)_6$	$K_3H_6R^{+3}(MoO_4)_6$
$K_5BW_{12}O_{40}\cdot 18H_2O$	$K_4SiMo_{12}O_{40}\cdot 18H_2O$	$K_6Te(MoO_4)_6$	$R^{+3} = Al^{+3}$, Fe^{+3}
$K_4SiW_{12}O_{40}\cdot 18H_2O$	$K_3AsMo_9O_{31}\cdot 14H_2O$	$K_4H_6Ni(MoO_4)_6$	Cr^{+3}, Mn^{+3}
$Na_3PW_{12}O_{40}\cdot 21H_2O$	etc.	$K_3AsO(MoO_4)_3$	etc.

The members of the 12-class are all similar to metatungstates; the free acids are easily prepared, very stable, and very easily crystallizable. The molybdenum compounds are almost without exception deep yellow in color. The members of the 6-class, on the other hand, show the reactions of the molybdate or tungstate ion, $[MoO_4]^{--}$ or $[WO_4]^{--}$. The molybdates are colorless when the central ion is colorless.

There is no doubt that Rosenheim has assigned the correct structures to the members of the 6-class. The complex anions are composed of MoO_4 or WO_4 tetrahedra. By sharing one corner, two of these tetrahedra form the ion $[Mo_2O_7]^{--}$, etc. By sharing a corner of each MoO_4 tetrahedron with the AsO_4 group, the ions $[AsO_3(MoO_4)]^{-3}$, $[AsO_2(MoO_4)_2]^{-3}$, $[AsO(MoO_4)_3]^{-3}$, $[As(MoO_4)_4]^{-3}$ may be formed. Similarly a central ion with coordination number of six can form an octahedron, all six corners of which may be shared with MoO_4 tetrahedra.

The Miolati-Rosenheim conception of the 12-acids is that they are similarly derived from the central groups $[H_2O_6]^{-10}$, $[BO_6]^{-9}$, $[SiO_6]^{-8}$, $[PO_6]^{-7}$, etc., by replacing the oxygen atoms by Mo_2O_7 or W_2O_7 groups. The corresponding acids are then written $H_{10}[H_2(W_2O_7)_6]$, metatungstic acid; $H_9[B(W_2O_7)_6]$, 12-tungstoboric acid; $H_8[Si(W_2O_7)_6]$, 12-tungstosilicic acid; $H_7[P(W_2O_7)_6]$, 12-tungstophosphoric acid; and similarly for the 12-molybdoacids. But the acids do not have the large number of replaceable hydrogen atoms indicated by these formulas. Their salts indicate that the true basicities are four less than this. Very many neutral salts corresponding to the formulas $H_6[H_2W_{12}O_{40}]\cdot xH_2O$, $H_5[BW_{12}O_{40}]\cdot xH_2O$, $H_4[SiW_{12}O_{40}]\cdot xH_2O$ and $H_3[PW_{12}O_{40}]\cdot xH_2O$ have been prepared, but only a few salts in which four more hydrogen atoms are replaced. These formulas, accepted by most investigators in this field,[9] no doubt represent correctly the number of replaceable hydrogen atoms, so that the Miolati-Rosenheim theory leads to incorrect results in this

[8] A. Rosenheim and J. Felix, *Z. anorg. Chem.*, 79,292 (1913).

[9] H. Copaux, *ibid.*, 74, 351 (1912); F. Kehrmann, *ibid.*, 39, 98 (1904); G. Wyrouboff, Bull. *soc. franc. min.*, 28, 239 (1905); etc.

respect. Rosenheim has contended that the ordinary salts are really acid salts, and he did succeed in replacing seven hydrogen atoms in 12-molybdophosphoric acid and 12-tungstophosphoric acid with guanidine. In other cases, however, guanidine replaces fewer hydrogen atoms than correspond to the Miolati-Rosenheim theory, so that the theory is not supported. Some salts of heavy metals also are known in which more hydrogen atoms are replaced than in the ordinary salts; these we consider to be basic salts.

The Miolati-Rosenheim theory offers no explanation of the characteristic properties of the 12-acids; for it involves the coordination about a central atom of six Mo_2O_7 or W_2O_7 groups, which are evidently identified with the bimolybdate and bitungstate ions, $[Mo_2O_7]^{--}$ and $[W_2O_7]^{--}$, and are hence composed of two MoO_4 or WO_4 tetrahedra with one corner shared. Accordingly they would be expected to show the reactions of the $[MoO_4]^{--}$ or $[WO_4]^{--}$ ion, and to belong to the same class as the 6-acids. In order to account for the pronounced differences between the 12-acids and the 6-acids there is needed a radical difference in structure, and this is not provided by the Miolati-Rosenheim theory.

3. The Structure of the 12-Tungstosilicate Ion and Related Ions

A set of principles underlying the formation of coordinated structures in crystals has been formulated and discussed in a previous paper.[10] These principles are also applicable in general to atom groups of finite extent. The following discussion illustrates their use in the deduction of the structures of highly complex ions.

Molybdenum and tungsten form tetrahedral ions, $[MoO_4]^{--}$ and $[WO_4]^{--}$, in which they have a coordination number of four. (It is probable that the metal–oxygen bonds in these ions are all of the shared electron pair type.) But the crystal radii[11] of the ions Mo^{+6} and W^{+6} are both about 0.62 Å., so that it is possible to group six oxygen ions, of crystal radius 1.35–1.40 Å., about one ion Mo^{+6} or W^{+6} at octahedron corners (Fig. 1). It is to be expected, then, that such an arrangement will also occur; and it has actually been shown to exist[12] in crystals of ammonium oxyfluomolybdate, $(NH_4)_3MoO_3F_3$, in which three oxygen ions and three fluorine ions are grouped about each molybdenum ion.

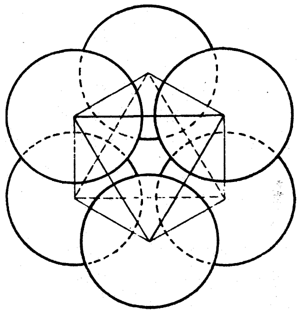

Fig. 1.—Six oxygen ions arranged at the corners of a regular octahedron about a tungsten or molybdenum ion.

Stable complexes may then be formed by arranging MoO_6 or WO_6 octahedra in such a way that they share corners with each other. The

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[10] Linus Pauling, THIS JOURNAL, 51, 1010 (1929).

[11] Linus Pauling, *ibid.*, 49, 765 (1927).

[12] Linus Pauling, *ibid.*, 46, 2738 (1924).

strength of the electrostatic bond from a hexavalent cation[13] to each corner of the octahedron of anions about it is 1, so that each oxygen ion will tend to be shared between two octahedra. On account of the large electric charge of the cations, the octahedra will share corners only, and not edges or faces.

A structure satisfying these requirements is shown in Fig. 2. Each octahedron shares three corners with adjoining octahedra, and has three unshared corners. The double negative charge of the oxygen ions at the unshared comers is not satisfied by the single molybdenum or tungsten electrostatic bond, of strength 1; in order that it be satisfied, each of these 36 oxygen ions must take up a hydrogen ion. The resultant $Mo_{12}O_{18}(OH)_{36}$ group is electrically neutral.

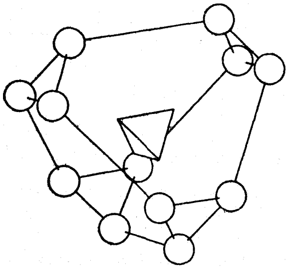

Fig. 2a.—Diagrammatic representation of a structure composed of twelve tungsten or molybdenum octahedra. Each octahedron is replaced by a circle. The lines connecting circles indicate that the corresponding octahedra are united through the possession of a common corner (an oxygen bond),

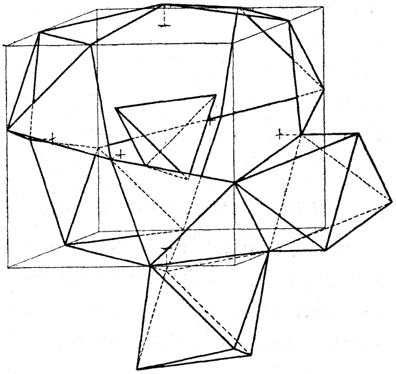

Fig. 2b.—The structure composed of twelve octahedra. Two octahedra are completely drawn. The face defined by the shared corners is shown for each of the others.

As a result of the strong repulsion between the adjacent highly charged cations the octahedra composing the group will be distorted. The distortion will take place in such a way that the Mo–O or W–O distance will remain approximately constant. The oxygen-oxygen distance determining the length of an octahedron edge is usually 2.70–2.80 Å., but may be as small as 2.50 Å. The mutual repulsion of the molybdenum or tungsten ions in the structure we are discussing will lengthen the three edges of each octahedron determined by the shared corners, the other edges being correspondingly shortened. In the crystals in which octahedron edges are shortened to 2.50 Å. (rutile, brookite, anatase, corundum),

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[13] Throughout this paper use will be made of the word ion, although it is recognized that the bonds may not approach the limiting case of purely ionic bonds very closely.

four edges at the most are so affected. In the MoO_6 and WO_6 octahedra nine edges are shortened by deformation, so that all of the oxygen ions are brought close together; it is probable that these nine edges will not be shorter than about 2.60 Å. If the metal-oxygen distances remain 2.00 Å. throughout, the other three edges are then about 3.10 Å. long, and the distorted octahedron has the appearance shown in Fig. 3.

As a result of this deformation, an additional oxygen ion at one corner of the tetrahedron of Fig. 2 would be reasonably close to three molybdenum or tungsten ions; in fact, if it remained at a distance of about 2.7 Å. from the oxygen ions at the shared corners of the octahedra, it would be about **3.0** Å. from the three metal ions. each of charge +6. These positions, in regions of positive potential, are accordingly stable ones for oxygen ions.

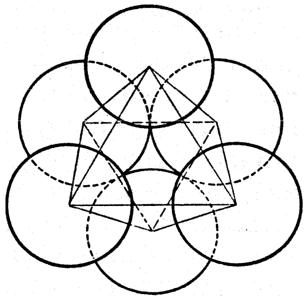

Fig. 3.—The distorted octahedron of oxygen ions about a tungsten or molybdenum ion.

It is also to be anticipated that the position in the region of negative potential at the center of the tetrahedron formed by these four oxygen ions would be stable for a small positive ion, such as B^{+3}, Si^{+4}, P^{+5}, As^{+5}, etc., with crystal radii 0.21, 0.41, 0.34 and 0.47 Å., respectively. For the strength of the electrostatic bond from Mo^{+6} or W^{+6} at the distance 3.0 Å. may be about $^1/_2$, in which case the three metal ions would not satisfy the charge of the oxygen ion and another positive ion would be required. If no other positive ion is available for this purpose, hydrogen ions would be used. The experimental observation that metatungstic acid is hexabasic indicates that two hydrogen ions are required for the four oxygen ions.

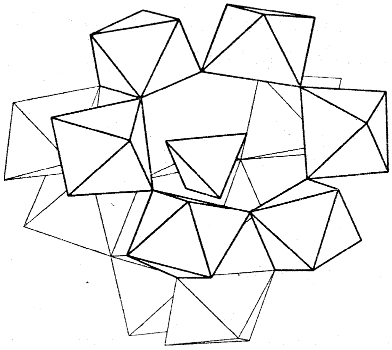

Fig. 4.—The structure of the 12-tungstosilicate ion and related ions. Twelve distorted octahedra (Fig. 3) are combined by sharing corners as shown. The tetrahedron represents the $[SiO_4]^{-4}$ ion. The complete structure has the composition $[SiO_4 \cdot W_{12}O_{18}(OH)_{36}]^{-4}$, and has the point-group symmetry T_d.

The completed complex ion, shown in Fig. 4, can now be described in the following way. Twelve molybdenum or tungsten octahedra combine by sharing corners occupied by oxygen ions (eighteen altogether). Each of the thirty-six unshared oxygen ions takes up a hydrogen ion to satisfy its negative charge. The resultant neutral structure is then stabilized by a central tetrahedral group $[RO_4]^{-3}$, with R = H_2^{++}, B^{+3}, Si^{+4}, P^{+5}, As^{+5}, etc. The central stabilizing group increases the stability of the complex not only by introducing negative ions in regions of large positive potential, but also by completing a structure which approximates close-packing of the large ions, each of the central oxygen ions being in contact with nine oxygen ions.

A first test of the possibility of existence of this structure is the investigation of the dimensions of the group of twelve octahedra to determine whether or not there is room for an RO_4 group within. In the $[SiO_4]^{-4}$ ion the oxygen-oxygen distance is about 2.60 Å., the silicon–oxygen distance being about **1.59 Å.**[14] The $[BO_4]^{-5}$, $[PO_4]^{-3}$ and $[AsO_4]^{-3}$ ions have about the same dimensions. Assuming three edges of each octahedron to be lengthened to **3.10 Å.**, each oxygen ion of the central RO_4 group will be about **2.85 Å.** from six oxygen ions in the surrounding structure. There is accordingly just room enough for the central tetrahedron. *A structure composed of less than twelve octahedra could not be built about the* R04 *group.*

A study of the structure has led to the conclusion that the deformation of the octahedra is not so great as that estimated to be the maximum possible. The nine short edges are probably about **2.65 Å.**, and the three long edges about **3.02 Å.** long. Each R04 oxygen ion is then about **2.77 Å.** from six oxygen ions of the surrounding structure, and about **3.14 Å.** from three W^{+6} or Mo^{+6} ions. The corresponding atomic positions are given by the following set of coordinates relative to orthogonal axes

1Si, B, P or As at 0 0 0
$4O_I$ at $u\,u\,u,\ u\,\bar{u}\,\bar{u},\ \bar{u}\,u\,\bar{u},\ \bar{u}\,\bar{u}\,u$, with $u = 1.59$ Å.
$6O_{III}$ at $t\,0\,0,\ 0\,t\,0,\ 0\,0\,t,\ \bar{t}\,0\,0,\ 0\,\bar{t}\,0,\ 0\,0\,\bar{t}$, with $t = 3.37$ Å.
$12O_{II}$ at $v\,v\,w,\ v\,\bar{v}\,\bar{w},\ \bar{v}\,v\,\bar{w},\ \bar{v}\,\bar{v}\,w$
$v\,w\,v,\ v\,\bar{w}\,\bar{v},\ \bar{v}\,w\,\bar{v},\ \bar{v}\,\bar{w}\,v$
$w\,v\,v,\ w\,\bar{v}\,\bar{v},\ \bar{w}\,v\,\bar{v},\ \bar{w}\,\bar{v}\,v$
with $v = 2.88$ Å. and $w = 0.74$ Å.

$12O_{IV}$ at $v\,v\,w$, etc., with $v = 2.55$ Å. and $w = 4.80$ Å.
12W or Mo at $v\,v\,w$, etc., with $v = 1.35$ Å. and $w = 4.00$ Å., about
$24O_{IV}$ at $x\,y\,z,\ z\,x\,y,\ y\,z\,x,\ y\,x\,z,\ x\,z\,y,\ z\,y\,x$
$x\,\bar{y}\,\bar{z},\ z\,\bar{x}\,\bar{y},\ y\,\bar{z}\,\bar{x},\ y\,\bar{x}\,\bar{z},\ x\,\bar{z}\,\bar{y},\ z\,\bar{y}\,\bar{x}$
$\bar{x}\,y\,\bar{z},\ \bar{z}\,x\,\bar{y},\ \bar{y}\,z\,\bar{x},\ \bar{y}\,x\,\bar{z},\ \bar{x}\,z\,\bar{y},\ \bar{z}\,y\,\bar{x}$
$\bar{x}\,\bar{y}\,z,\ \bar{z}\,\bar{x}\,y,\ \bar{y}\,\bar{z}\,x,\ \bar{y}\,\bar{x}\,z,\ \bar{x}\,\bar{z}\,y,\ \bar{z}\,\bar{y}\,x$
with $x = 0.02$ Å., $y = 5.28$ Å., and $z = 1.90$ Å.

4. The Properties of the 12-Tungsto- and Molybdoacids

The structure proposed for the 12-tungsto- and molybdoacids, in which the tungsten and molybdenum atoms have a coordination number of six, requires, in agreement with experiment, that these substances have

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[14] These distances *are* in agreement with those found experimentally for orthosilicates.

distinctly different properties from the ordinary tungstic and molybdic acids, with coördination number four.

Formulas for the tungsten acids corresponding to the proposed structure are

$H_6[H_2O_4{\cdot}W_{12}O_{18}(OH)_{36}]$, metatungstic acid
$H_5[BO_4{\cdot}W_{12}O_{18}(OH)_{36}]$, 12-tungstoboric acid
$H_4[SiO_4{\cdot}W_{12}O_{18}(OH)_{36}]$, 12-tungstosilicic acid
$H_3[PO_4{\cdot}W_{12}O_{18}(OH)_{36}]$, 12-tungstophosphoric acid

Similar formulas are to be ascribed to the molybdenum acids. *The numbers of replaceable hydrogen atoms given by these formulas are exactly those found experimentally.* This is a consequence of the fact that the coordinated structure surrounding the central RO_4 group is electrically neutral, so that the complex anion has the same charge as the RO_4 group itself; in other words, the heteropolyacid has the same number of replaceable hydrogens as the acid from which it was derived.

A further notable feature of the proposed structure is the large amount of water of constitution, amounting to $18H_2O$ per molecule, aside from the replaceable hydrogen of the acids and the central hydrogen of the metatungstates and the corresponding molybdates. This explains the high water content characteristic of these compounds, which had long been an unsolved puzzle. The water content of the heteropolyacids was studied by Rosenheim and Jaenicke,[3f] who found the results given in Table I. There is some doubt as to the exact amount of water in many cases; for example, previous investigators had assigned $31H_2O$ to the series of crystals corresponding to the first column, instead of $30H_2O$.

TABLE I

WATER CONTENTS OF HETEROPOLYACIDS

$H_6[H_2W_{12}O_{40}]$	..	$24H_2O$	14–17 H_2O (?)
$H_5[BW_{12}O_{40}]$	$30H_2O$	$\boxed{24}$	12
$H_4[SiW_{12}O_{40}]$	30	24	$\boxed{22}$
$H_3[PW_{12}O_{40}]$	30	24	21
$H_4[SiMo_{12}O_{40}]$	30	..	14
$H_3[PMo_{12}O_{40}]$	30	24	14 (?)

The 30- and 24-hydrates are compatible with our formulas. We would say that eighteen molecules of water is water of constitution, and that $12H_2O$ or $6H_2O$ only is water of crystallization, that is, water which fills the interstices which result from piling together the large constituent groups in the construction of the crystals. It is to be expected that usually there will be some water of crystallization, on account of the shape of the complex anions.

Four[15] of the hydrates of the third column contain less than $18H_2O$.

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[15] Two of these could not be identified with certainty as distinct compounds.

These substances are, however, different from the others in their properties. Rosenheim and Jaenicke state that they dehydrate on heating without melting, whereas the others show definite melting points. They can be prepared only under dehydrating conditions—by crystallizing out of concentrated nitric acid, or by heating the higher hydrates to constant weight at temperatures above their melting points. These properties are to be expected from the proposed structure, assuming that dehydration consists in the sharing of corners between octahedra in different complexes, with the elimination of $1H_2O$ for each shared corner. The coordination bonds introduced between the complexes in this way tie the whole crystal together, and prevent it from melting at a low temperature. The presence of compounds with over $18H_2O$ in this column is not surprising; they contain less than 18 molecules of water of constitution, and in addition some water of crystallization.

The 30-hydrates are all isomorphous, and so are the 24-hydrates, with the exception of the tungstoboric acid. This tungstoboric acid and the tungstosilicic acid of the third column are isomers of the ordinary heteropolyacids; their structure is discussed in the following section.

The existence of 18 molecules of water of constitution is further indicated by the data on salts, most of which crystallize with $18H_2O$ or more. For example, Groth[16] lists seventy-seven salts of 12-tungstosilicic acid which have been subjected to crystallographic examination. Of these all but thirteen contain $18H_2O$ or more, the exceptional ones having $13–17H_2O$.

The 12-heteropolyacids and their salts have a pronounced tendency to form cubic or pseudocubic crystals; thus about two-thirds of the 12-tungstosilicates with $18H_2O$ or more are cubic or pseudocubic (Table 11), and the other acids and their salts crystallize similarly. The structure proposed for these complex anions has the symmetry of the cubic point-group T_d. Accordingly cubic crystals of simple structure, containing as little as one complex anion in the unit of structure, can be built of these groups, and such crystals would be expected to occur. If, on the other hand, the complex anion did not possess cubic symmetry, a very large unit of structure would be required in a cubic crystal, and these crystals would be the exception and not the rule. It is also significant that salts with less than $18H_2O$ are all triclinic or monoclinic and show no pseudocubic development. Further similar evidence for 18 molecules of water of constitution and for the cubic point-group symmetry of the complex anions is provided by the three tungstophosphates listed by Groth.[17] The salt with less than $18H_2O$, $Na_3PW_{12}O_{40}\cdot 15H_2O$, is triclinic, while $Na_3PW_{12}O_{40}\cdot 21H_2O$ and $Ba_3(PW_{12}O_{40})_2\cdot 48H_2O$ form cubic crystals.

[16] Groth, "Chemische Kristallographie," Engelmann, Leipzig, 1908, Vol. II.

[17] Groth, Ref. 16, Vol. II, pp. 883–884.

TABLE II

CRYSTALLINE FORM OF 12-TUNGSTOSILICATES

No.		
1	Triclinic or monoclinic	$Na_4X \cdot 20H_2O$ ($X = [SiW_{12}O_{40}]^{-4}$) $R_2X \cdot 18H_2O$; R^{+2} = Ca, Mg, Mn, Ni, Co, Zn $Pb_2X \cdot 21H_2O$ $Sr_2X \cdot 23H_2O$ $Cd_2X \cdot 22H_2O$ $InHX \cdot 20H_2O$ $R_4X_3 \cdot 60H_2O$; R^{+3} = Al, Cr, Ga, Bi $In_4X_3 \cdot 63H_2O$ $RHX \cdot 18H_2O$; R^{+3} = La, Ce, Di, Gd $RHX \cdot 24\frac{1}{2}H_2O$; R^{+3} = Y, Tb, Yb
2	Hexagonal—$a:c$ = 1:0.6585	$K_4X \cdot 18H_2O$
3	Tetragonal—$a:c$ = 1:1.0117 (pseudocubic)	$H_4X \cdot 30$ or $31H_2O$
4	Trigonal—a! = 86° 26′–89° 8′ (pseudocubic)	$Li_4X \cdot 24H_2O$ $R_2X \cdot 24H_2O$; R^{+2} = Ca, Ba $H_4X \cdot 24H_2O$
5	Trigonal[a]—α = 75° 43′–77″ 18′	$R_4X_3 \cdot 78H_2O$; R^{+3} = Nd, Di, Sm, Gd, Y, Tb, Yb
6	Trigonal—a = 56° 4′–57° 30′ (pseudocubic)	$R_2X \cdot 27H_2O$; R^{+2} = Ca, Sr, Mg, Mn, Ni, Co, Cu, Zn, Cd $Be_2X \cdot 29H_2O$ $R_4X_3 \cdot 87H_2O$; R^{+3} = Al, Cr, Ga $R_4X_3 \cdot 81H_2O$; R^{+3} = La, Ce, Di, Sm, Gd $Gd_4X_3 \cdot 90H_2O$ $ThX \cdot 27H_2O$ $ThX \cdot 30H_2O$
7	Cubic	$Be_2X \cdot 31H_2O$ $R_4X_3 \cdot 93H_2O$; R^{+3} = Al, Cr, Fe, Ga, In

[a] These crystals, while not pseudocubic in their face development, have axial ratios in the neighborhood of 1:3, and so may have a pseudocubic structure.

5. Iso-12-Tungstosilicic Acid and Iso-12-Tungstoboric Acid

There exist in addition to the 12-acids just discussed acids of the composition $H_4(SiW_{12}O_{40}) \cdot xH_2O$ and $H_5(BW_{12}O_{40}) \cdot xH_2O$ which differ from them in their reactions, and are called iso-12-acids. Iso-12-tungstosilicic acid and its salts were discovered and investigated by Marignac.[18] Iso-12-tungstoboric acid, previously studied by Copaux,[19] was assigned its accepted formula and further studied by Rosenheim.[20] The iso-acids retain their identity on solution and recrystallization, and on conversion into salts and again into acids. They are prepared by heating solutions of the normal acids to dryness and are also formed to some extent in the preparation of the normal acids and their salts.

The Miolati-Rosenheim theory[Z1] has been made to account for the existence of two forms of 12-tungstosilicic and 12-tungstoboric acid by

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[18] C. Marignac, *Ann. chim. phys.*, [4] 3, 5 (1864).

[19] H. Copaux, ibid., [8] 17, 217 (19C9).

[20] A. Rosenheim, Z. anorg. *Chem.*, **70**, 418 (1911); A. Rosenheim and J. Jaenicke, *ibid.*, **101**, 235 (1917).

[21] A. Rosenheim and J. Jaenicke, *ibid.*, 100, 304 (1917); P. Pfeiffer, *ibid.*, **105**, 26 (1918).

assuming a difference in character of some of the six positions about the central atom and the others.

The method of formation of the iso-acids by heating the normal acids suggests a condensation of the normal complex anions with the liberation of water of constitution. The ease of solution and reprecipitation of the iso-acids requires that the constituent coordinated groups be not too large. A structure satisfying these requirements is obtained by combining two $[RO_4W_{12}O_{18}(OH)_{36}]^{-z}$ groups in such a way that six octahedra of one group share one corner apiece with six octahedra of the other group. The resultant anion is shown in Fig. 5. The acids would then have the formulas

$$H_8[(SiO_4)_2W_{24}O_{42}(OH)_{60}] \text{ or } H_4[SiW_{12}O_{40}]\cdot 15H_2O$$
$$H_{16}[(BO_4)_2W_{24}O_{42}(OH)_{60}] \text{ or } H_5[BW_{12}O_{40}]\cdot 15H_2O$$

The amount of water of constitution, $15H_2O$, required by this structure is compatible with the observed hydration of the acids, $24H_2O$ and $22H_2O$ (Table I), for it is to be expected that some water of crystallization will also be present.

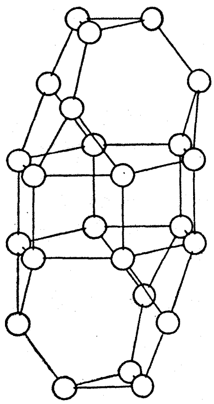

Fig. 5a.

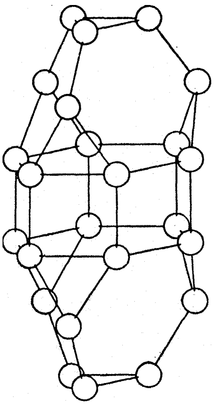

Fig. 5b.

Fig. 5a.—A possible structure for the iso-12-polyacid ion, made from two ions of Fig. 4 by the elimination of $6H_2O$ and the formation of six oxygen bonds. Point-group symmetry D_{3d}.

Fig. 5b.—The probable structure of the iso-12-polyacid ion. Point-group symmetry D_{3h}.

The salts of these acids also usually crystallize with over $15H_2O$. The well-investigated crystals $K_4SiW_{12}O_{40}\cdot 9H_2O$ (rhombic) and $Na_4SiW_{12}O_{40}\cdot 12H_2O$ (trigonal) are exceptions. It is probable that further dehydration, with the accompanying sharing of octahedron corners between the iso-anions, has taken place here.

The iso-anion $[(RO_4)_2W_{24}O_{42}(OH)_{60}]^{-2z}$ has the symmetry of the point-group D_{3d} (Fig. 5a), or, more probably, D_{3h} (Fig. 5b). Verification of the proposed structure will be attempted through the investigation with x-rays of the hexagonal bipyramidal crystals of iso-12-tungstoboric acid, $H_5[BW_{12}O_{40}]\cdot 24H_2O$.

6. The Unsaturated or Condensed Heteropolyacids

There also exist heteropolyacids, similar in their reactions to the saturated 12-heteropolyacids, in which the number of tungsten or molybdenum atoms per central atom is less than twelve. It is probable that the anions of these acids are formed from the 12-anions by the sharing between two groups of some complete octahedra. The 12-octahedra groups are of such a nature that two can combine by sharing six octahedra, as shown in Fig. 6, or by sharing two octahedra.

The acids formed from the 12-acids of phosphorus or arsenic would have formulas of the type

$$H_6[(PO_4)_2W_{18}O_{30}(OH)_{48}] \text{ or } H_6[P_2W_{18}O_{62}]\cdot 24H_2O$$

These acids should then have six replaceable hydrogen atoms and contain 24 molecules of water of constitution.

Phosphorus and arsenic form 9-acids with both molybdenum and tungsten very easily.[22] (It is, indeed, reported to be difficult to prepare salts of the saturated arsenic acids, and the acids themselves are unknown.) Most of the salts of these acids are formed by replacing six hydrogen atoms, although in a few twelve hydrogen atoms are replaced. The basicity of the acids accordingly agrees with the structure suggested.

The crystallized free acids, of composition $H_6[P_2W_{18}O_{62}]\cdot 39H_2O$, $H_6[As_2W_{18}O_{62}]\cdot 39H_2O$, $H_6[P_2Mo_{18}O_{62}]\cdot 33$ or $37H_2O$ and $H_6[As_2Mo_{18}O_{62}]\cdot 25$ or $29H_2O$, all possess some water of crystallization in addition to the water of constitution. This is true also of a majority of the salts; in the exceptional cases the amount of constitutional water is diminished by the sharing of corners of octahedra in different complex anions.

The anions of formula $[(PO_4)_2W_{18}O_{30}(OH)_{48}]$, etc., have the symmetry of the point-group D_{3d}. Verification of this should be possible through the examination with x-rays of the dihexagonal bipyramidal crystals $K_6P_2W_{18}O_{62}\cdot 28H_2O$, $K_6As_2Mo_{18}O_{62}\cdot 28H_2O$ and $Na_6As_2Mo_{18}O_{62}\cdot 30H_2O$.[23]

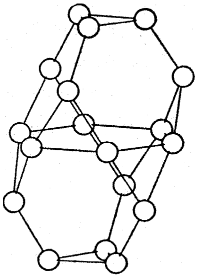

Fig. 6.—The probable structure of the 9-polyacid ion, formed from two ions of Fig. 4 by the sharing of six octahedra. Point-group symmetry D_{3d}. The structure of point-group symmetry D_{3h} (the analog of Fig. 5b) is probably unstable.

It is possible that each anion of the compounds with 11:1 as the ratio of the number of molybdenum or tungsten atoms to the number of central atoms is formed from two 12-anions with two octahedra in common, and that the anions of the compounds reported with ratios 10:1, 21:2 and 17:2 are composed of more than two 12-anions combined by sharing octahedra. In these cases, however, the confident assignment of specific structures must follow further experimental investigation.

Summary

There is described a structure for the 12-heteropolyacids of molybdenum and tungsten derived by the application of the principles under-

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[22] A. Rosenheim and J. Jaenicke, *Z. anorg. Chem.*, 101,235 (1917); A. Rosenheim and A. Traube, *ibid.*, 91, 74 (1915).

[23] Groth, Ref. 16, Vol. II, p. 879.

lying the formation of coordinated structures in complex crystals. The proposed structure, shown in Fig. 4, may be represented by formulas such as $H_4[SiO_4 \cdot W_{12}O_{18}(OH)_{36}]$. It correlates the characteristic differences between the properties of the 12-molybdo- and tungsto-acids and those of the $[MoO_4]^{--}$ and $[WO_4]^{--}$ ions with the existence of molybdenum and tungsten atoms with coordination numbers 6 and 4, respectively, in these two types of compounds. It leads to a number of replaceable hydrogen atoms in agreement with experiment, and accounts for the large water content of the acids and their salts. The cubic point-group symmetry of the suggested structure for the complex anions explains the tendency of these compounds to form cubic or pseudocubic crystals.

The iso-12-tungstosilicate and iso-12-tungstoborate ions are ascribed the structure shown in Fig. 5, in which two 12-anions are combined through the formation of oxygen bonds.

A structure for one class of unsaturated acids, corresponding to formulas such as $H_6[(PO_4)_2 \cdot W_{18}O_{30}(OH)_{48}]$, is also suggested, involving the combination of two 12-anions as shown in Fig. 6. Possible structures for other unsaturated acids are indicated.

Among the predictions made on the basis of the proposed structure and susceptible to experimental investigation are the following: that the normal 12-anions have the point-group symmetry T_d, and the iso-12-anions and the 9-anions the symmetry D_{3d} or D_{3h}; that the normal 12-acids have a molecular weight corresponding to one RO_4 group per complex, and the iso-12-acids and 9-acids to two; and that the constituent atoms in the complexes occupy certain positions relative to each other, such that each tungsten or molybdenum atom has a first coordination shell of six oxygen atoms none of which is part of the central RO_4 group.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL AND PHYSICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

THE CRYSTAL STRUCTURE OF META-IODOBENZOIC ACID[1]

BY HAROLD P. KLUG, EDWARD MACK, JR., AND F. C. BLAKE

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We have been led to an x-ray examination of the crystals of a number of benzene derivatives in connection with a study of vapor pressures and heats of vaporization. It seems worth while at this time to report the crystal structure which we have found for m-iodobenzoic acid, especially since the solution obtained seems to be unique, and very few unambiguous solutions have been reported for organic compounds crystallizing in the

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[1] An abstract of a thesis presented by H. P. Klug in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Ohio State University in June, 1928.

monoclinic system. m-Iodobenzoic acid is a particularly interesting case because of the fact that it is so nearly orthorhombic, the angle β being **91°** 29.5'. When β is so slightly different from a right angle, it is difficult to identify the reflections from certain sets of planes, namely, the pyramids and orthodomes.

m-Iodobenzoic acid was prepared by the method of O. Grothe,[2] which consists of the hot diazotization of a strong solution of *m*-aminobenzoic acid in dilute sulfuric acid mixed with a concentrated solution of potassium iodide in excess. The yield was very poor (less than 5%). The crude product was purified by two vacuum sublimations; this gave a product with a melting point of **186.6–186.8".** Crystals grown from ether were well-formed, flat needles, showing the (0 0 1) face.

Groth[3] gives the following data on the crystal: a : b : c = 1.3450 : **1 : 5.6247;** $\beta = 91° 29.5'$; m. p. 185°; sp. gr. **2.171.**

Preparation of X-Ray Photographs and Their Analysis for Data.— Data for the analysis of this crystal were obtained by means of the powder, Laue and oscillated crystal methods. Photographs were taken **and** the usual measurements and calculations made.

In the powder method sodium chloride was used as a comparison standard. The m-iodobenzoic acid was powdered to pass through a 200-mesh sieve and the glass capillary tube was oscillated through an angle of **15"** during exposure to the molybdenum K_α doublet from a water-cooled Coolidge tube. The exposure was for twenty-six hours at 35 kilovolts with a current of **18** milliamperes. Distances on the film could be measured to within 0.002 cm. Blake's[4] correction constant, **3** cot 8 d θ, for powder films was used in all the calculations. Using the crystallographer's orientation and notation, Wyckoff's quadratic[5] form of the equation for the monoclinic unit becomes, when squared and solved for $\sin^2$ 8

$$\sin^2\theta = \frac{\lambda^2}{b_0^2}\left\{\frac{h^2}{4a^2\sin^2\beta} + \frac{l^2}{4c^2\sin^2\beta} \pm \frac{hl\cos\beta}{2ac\sin^2\beta} + \frac{k^2}{4}\right\}$$

If we designate the bracketed term by L, then

$$L = \frac{\sin^2\theta\, b_0^2}{\lambda^2}$$

The thirteen lines measurable on the powder photographs could all be accounted for only on the assumption of a 4-molecule cell.

The agreement between the observed and calculated values of L is excellent.

Laue photographs were taken perpendicular to the (0 0 1) face and at small angles to the perpendicular, with the general radiation from a tung-

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[2] **O.** Grothe, **J.** *prakt. Chem.*, [2] 18,324 (1878).

[3] Groth, "Chemische Kristallographie," Engelmann, Leipzig, 1906, Vol. 4, p. 466.

[4] Blake, Phys. Rw., *26*, 60–70 (1925).

[5] Wyckoff, "Structure of Crystals," Chemical Catalog Co., Easton, Pa., 1924, p. 98.

TABLE I

DATA FROM A *m*-IODOBENZOIC ACID POWDER PHOTOGRAPH

Indices h *k* *l*	L obs.	L[a] calcd.	Indices *h* *k* *l*	L obs.	L[a] calcd.
0 0 4	0.1302	0.1284	$\bar{1}$ 1 3	0.4587	0.4595
1 0 1	.1521	.1523	1 1 4	.5255	.5279
1 0 3	.2240	.2201	$\bar{1}$ 0 7		.5236
0 0 6	.2914	.2890	$\bar{1}$ 0 9	.7744	.7770
$\bar{1}$ 0 5	.3314	.3344	$\bar{1}$ 1 7		.7736
1 0 5	.3515	.3520	2 1 1	.8376	.8313
1 1 0	.3934	.3925	$\bar{2}$ 1 2		.8449
1 1 2	.4271	.4281	2 1 3	.9097	.9027

[a] The calculated values of L are purely theoretical values obtained by substituting the crystallographic data in the bracketed term of the above equation. The observed values of L are obtained from the values of θ from measurements of the powder photographs.

sten target at 54–55 kilovolts, 14 milliamperes and for two and one-fifth hours. The crystal to film distance was 5 cm. for all photographs.

The oscillated crystal photographs were taken with the K_α doublet from a molybdenum target at 55 kilovolts, 19 milliamperes, for twenty-four to twenty-six hours. In addition to the usual method of calculating angle θ for each reflection, the indices of the planes reflecting were checked by means of Bernal[6] diagrams. The analysis shows unequivocally that the cell contains four molecules. The large number of reflections gives the data necessary for space-group determination.

Correction of the Axial Ratio.—On some of the oscillated crystal photographs where the reflections were unusually sharp and distinct, and therefore capable of quite accurate measurement, the agreement between the two values of L was not what it should have been. This might have been due to a slight inaccuracy in the axial ratio. Since there could be no doubt about the correctness of the various orders of (0 0 1) found on one of the films, and also of the various reflections of (0 1 l) in the first layer line above and below, it was decided to use them as a basis for correcting the axial ratio. The new axial ratio, then, assuming that β is correct as given, is

$$a : b : c = 1.3252 : 1 : 5.5824$$

The size of unit cell is

$$a_0 = 6.206,\ b_0 = 4.683,\ c_0 = 26.14\ \text{Å}.$$

All of the data for the oscillated crystal and powder photographs were recalculated on the basis of this new axial ratio; the agreement between the theoretical and observed values was remarkably good for all except a few lines out of several hundred.

Absorption in the Crystal and a New Use of Filters in Laue Photograph Technique.—The critical absorption limit for the strongly absorbing iodine falls at 0.37 Å. It might be expected that the iodine would absorb

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[6] Bernal, *Proc. Roy. Soc. London*, **113A**, 117 (1927).

most or all of the wave lengths below its critical absorption limit. Then the calculated values of $n\lambda$ for the Laue photographs would show no values below 0.37 Å. for the correct cell, Inspection of the data showed this to be the case for a four molecule cell.

Some method was then needed to determine whether the assumption that the iodine absorbed all wave lengths below 0.37 Å. was justified. The critical absorption limit for tin lies just above that for iodine, being at 0.42 Å. If a filter of tin of sufficient thickness to cut out all wave lengths below its critical absorption limit were used, a Laue photograph might be taken without the absorption of the iodine being a factor. Since the lower wave length limit would be known accurately, there would be no doubt as to the true size of the unit cell. The thickness of pure tin foil necessary to absorb nine-tenths of the radiation in those wave lengths below 0.37 Å. was calculated with the Wyckoff[7] and Compton[8] modifications of the absorption equation. In the former case the calculated thickness was 0.0082 cm., in the latter 0.0087 cm. The filter actually used was 0.0085 cm. in thickness. It was assumed that if the absorptive power of the iodine approached the value it was supposed to have, it would absorb the other tenth of the radiation below 0.37 Å.

To check the efficiency of this filter, reflection photographs from the (10 0) face of rock salt were taken, with and without the filter. The salt crystal was oscillated through an angle of 40° during the exposure. The α_1, β_1, β_2, β_3, β_4, γ_1, γ_2 and γ_3 lines of the L spectrum of tungsten appeared on the photograph taken without the filter. These lines were used for calibration of the camera. The tube was working under the same voltage and current as during the taking of the Laue photographs. The photograph without the filter showed the low wave length limit to be at 0.31 Å. instead of 0.25 Å. This probably indicates a peak in the transformer curve. The silver absorption edge was found at 0.47 Å., the bromine edge at 0.91 Å. and the weaker second-order silver edge at 0.96 Å. The photograph taken with the filter showed a very faint radiation up to the absorption edge for tin at 0.41 Å. The second-order tin absorption edge was found to correspond with 0.83 Å.

Inspection of the photograph taken without the filter confirmed the assumption that the iodine atoms might completely absorb the radiation below 0.37 Å., for the radiation is comparatively weak below this. A Laue photograph was taken using the filter. It was analyzed in the same manner as the others, and proved that the unit cell contained four molecules, there being no values of $n\lambda$ below 0.42 Å.

Wyckoff[9] discusses the use of filters to obtain a more desirable distribu-

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[7] Wyckoff, ref. 5, p. 83.

[8] Compton, "Bulletin of the National Research Council," No. 4, 1920.

[9] Wyckoff, *Am. J. Sci.*, [4] **50**, 339 (1920).

tion of wave lengths for Laue photographs, and concludes that their use is not desirable. Their use in the manner just described, however, seems a valuable addition to Laue photograph technique.

Determination of the Space-Group.—Inspection of the data showed that all types of planes were present except $(h\ 0\ l)$ when $(h + l)$ is odd. Since these are the only abnormalities, the basic lattice is the simple Γ_m lattice of Bravais and not Γ'_m. Astbury and Yardley[10] have tabulated the data for the examination of the 230 space-groups by x-rays. In the monoclinic sphenoidal class there are only two space-groups, C_2^1 and C_2^2, based on the Γ_m lattice. The first of these has no abnormal spacings and the latter only (0 1 0) halved. The class, therefore, cannot be sphenoidal, as given by Groth. The molecules of m-iodobenzoic acid are most certainly asymmetric, and there are four of them in the unit cell. Thus the class cannot be domatic. This leaves the two space-groups C_{2h}^4 and C_{2h}^5 in the prismatic class as the only possibilities. These two groups are the same except that the symmetry axis is a screw axis in C_{2h}^5 and therefore (0 1 0) is also halved in this space-group. Examination of the powder photograph showed that (0 1 0), which should have fallen between (1 0 3) and (0 0 6), was missing. Therefore, (0 1 0) is halved and the space-group is C_{2h}^5. C_s^2 does not have (0 1 0) halved, and this is further proof that the class cannot be domatic.

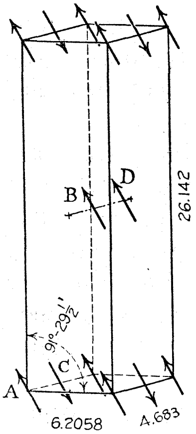

Fig. 1.

Determination of Parameters.—The space-group C_{2h}^5 contains a plane of symmetry and a screw axis of symmetry. This means that if one of the molecules is placed at the corners of the lattice, the second molecule is obtained from it by reflection in a plane perpendicular to the b axis, plus possible translations parallel to the a and c axes. The other two molecules are obtained by rotating these two through 180°, plus a translation along the b axis.

The coordinates of the equivalent points of the four molecules in the unit cell, relative to the crystallographic axes, are (0 0 0), $(^1/_2\ v\ ^1/_2)$, $(u\ ^1/_2\ w)$, $(u + {^1/_2},\ v + {^1/_2},\ w + {^1/_2})$. These are equivalent to the positions given by Wyckoff,[11] for in his notation the b and c axes have been interchanged. Also the *a* and *c* axes in the monoclinic system are interchangeable.

The determination of the variable parameters u, v and w can be accomplished with a fair degree of accuracy from the data on the oscillated crystal photographs. The presence on one of the photographs of extremely strong reflections for (10 1), (10 3), (10 5), (10 7), (10 9), (10 11), and for

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[10] Astbury and Yardley, *Phil. Trans. Roy. Soc. London*, **224A**, 221–257 (1924).

[11] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Carnegie Institute Publication No. 318, Washington, 1922, p. 151.

the corresponding planes where l is negative, make it extremely probable that u and w are equal to 0. The coördinates then become: (0 0 0), ($^1/_2\ v\ ^1/_2$), (0 $^1/_2$ 0), ($^1/_2\ v + ^1/_2\ ^1/_2$).

The positions of the molecules within the cell are shown in Fig. 1. The B molecule is obtained from the A molecule by reflection and translations parallel to the *a* and c axes. The C and D molecules are obtained from A and B, respectively, by rotation through 180° and a translation along the b axis.

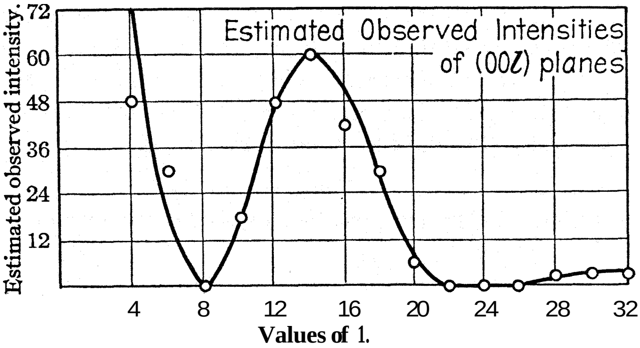

Fig. 2.—Estimated observed intensities of (0 0 l) planes.

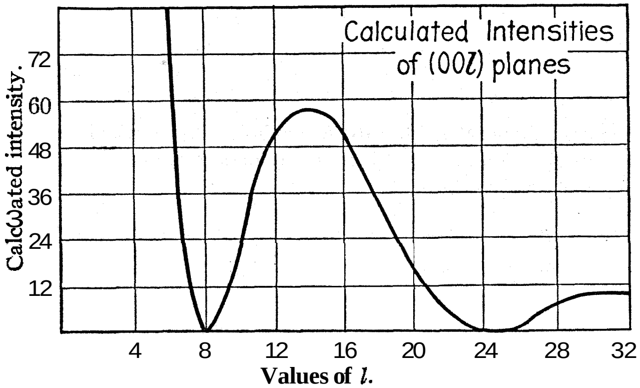

Fig. 3.—Calculated intensity of (0 0 l) planes.

The test of the correctness of these positions is whether the theoretically calculated values of the intensities of reflection check the actual intensities on the photographs. Wyckoff[12] gives the following expression for the intensity of x-ray reflection

$$I \propto \left(\frac{d_{hkl}}{n}\right)^{2.35} \left\{ [\Sigma \overline{N}_s \cos 2\pi n\ (hx_s + ky_s + lz_s)]^2 + [\sum_s \overline{N}_s \sin 2\pi n\ (hx_s + ky_s + lz_s)]^2 \right\}$$

It would be hopeless to attempt to compare in this manner the intensities for each of the several hundred reflections appearing on the films, but it

[12] Wyckoff, ref. 5, p. 107.

may be done for a few important sets of planes. In Fig. 2 is shown a graph of the estimated intensities of the various orders of (0 0 1) plane from one of the oscillated crystal photographs. It will be seen that the curve shows a minimum point at (0 0 8) and a maximum at (0 0 14). This would indicate that there must be another molecule or a periodicity along the *c* direction at a distance of approximately $^1/_{14}$ to $^1/_{16}$. The structure factors, $(A2 + B^2)$, for the even-order (0 0 1) planes were calculated, and from these the theoretical intensities were determined. It was assumed in these calculations that the molecule, as a whole, reflected from its center of gravity. Also the factor $\overline{N}_s$ was dropped since it is a constant throughout the calculations. The theoretical curve of the intensities is given in Fig. 3. The assumption has been made that this *z* parameter is $^1/_{16}$. The agreement between the two curves is good. The data for these curves are given in Table II.

TABLE II

INTENSITY DATA FOR (0 0 *l*) PLANES FROM OSCILLATED CRYSTAL PHOTOGRAPH NUMBER 3

Plane	Estimated obs. intens.	Calculated intensity	Plane	Estimated obs. intens.	Calculated intensity
0 0 2	[a]	5758	0 0 1 8	30	33
0 0 4	48	661	0 0 2 0	6	15
0 0 6	30	75	0 0 2 2	0	4
0 0 8	0	0	0 0 2 4	0	0
0 0 1 0	18	23	0 0 2 6	0	2
0 0 1 2	48	51	0 0 2 8	3	7
0 0 1 4	60	59	0 0 3 0	3	10
0 0 1 6	42	51	0 0 3 2	3	10

[a] 0 0 2 is missing from the film because of a hole in the back of the camera where the undeviated beam passed out. 0 0 4 is probably underestimated in intensity on account of blackening near undeviated beam.

Thus a periodicity along the *c* axis equal to approximately $^1/_{16}$ of its length is reasonably certain. W. H. Bragg[13] has recently been able to explain the observed intensities of the reflections from the various planes of naphthalene, on the basis of a periodicity within the molecule. An examination of a model of the molecule of *m*-iodobenzoic acid reveals some interesting things in this respect. The model, embodying the "puckered" benzene ring, may be approximately represented (to scale) by the drawing in Fig. 4. The center of gravity of the ring and the rest of the molecule is approximately at M. Since their weights are so nearly the same (I = 127) and the rest of the ring = 121, the center of gravity of the whole molecule will be approximately at P on the line joining the centers of gravity of the two parts. If it is assumed that the carboxyl group is disposed approximately as shown in Fig. 4, and that the distance between the centers of the carbon and iodine atoms is approximately 1.54/2 + 2.788/2 Å.,[14] and that

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[13] W. H. Bragg, *Z. Krist.,* 66, 22 (1927).

[14] Harris, Mack and Blake, THIS JOURNAL, 50,1595 (1928).

the molecule is located with respect to the c-axis as shown, then the projected distance along the *c* axis between P and M or between P and I is very nearly 1.65 Å., which is about $^1/_{16}$ of the length of the cell. The general pattern of the reflections occurring is probably set up by the molecule as a whole, and may be thought of as originating from the center of gravity, P. The points M and I would also set up reflections which will be in phase with each other but will be completely out of phase with those from P for (0 0 8). Since their sum is equivalent to the reflection from P, (0 0 8) will he missing. In the neighborhood of (0 0 16) they will be in phase with P and make these reflections unusually strong. Thus the intensities for the (0 0 *l*) planes may be readily explained.

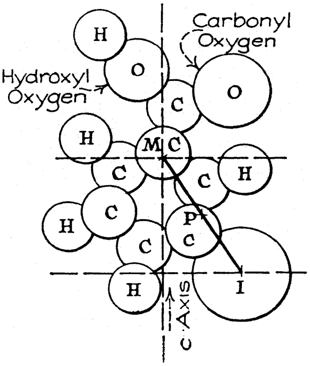

Fig. 4.

To determine the value of the parameter v along the b axis the (0 1 1) and (0 $\bar{1}$ *l*) reflections on film Number 3 were taken. Examination of the film shows that in general those reflections are weaker where *l* is even. This would indicate that the value of v must be nearly $^1/_2$. The structure factors for this set of planes were calculated and the intensities determined. The periodicity along the *c* axis had to be taken into account here, too, and with respect to this set of planes it is approximately $^1/_{12}$. Table III gives the observed and calculated intensities of this set of planes. It will be seen that the observed intensities agree only roughly with the calculated intensities. This is because the C molecule falls half way along the b axis. It is not equivalent to the A and B molecules in its effect on the x-ray beam. If it were equivalent the first order of (0 1 1) would be missing completely, whereas it is present but greatly reduced in intensity. (0 1 2) has its intensity increased considerably because of the C molecule. (0 1 3) is reduced in intensity for the same reason as (0 1 1). Beyond this the effect of the C molecule is still noticeable but not quite so great. We are not able to take it into account quantitatively in the determination of the theoretical

TABLE III

INTENSITY DATA FOR (0 1 *l*) PLANES FROM OSCILLATED CRYSTAL PHOTOGRAPH NUMBER 3

Plane	Estimated obs. intens.	Calculated intensity	Plane	Estimated obs. intens.	Calculated intensity
0 1 1	6	482	0 1 8	8	4
0 1 2	16	37	0 1 9	10	60
0 1 3	12	197	0 1 10	4	8
0 1 4	10	9	0 1 11	10	77
0 1 5	15	17	0 1 12	4	8
0 1 6	0	0	0 1 13	6	57
0 1 7	12	12	0 1 14	4	4

intensities. The best value for the parameter v is approximately $^4/_{10}$. The data on these planes are given in Table III.

Model **of the Unit** Cell.—A model was made by constructing molecules to scale from wooden balls as shown in Fig. 4. These were then placed at the positions of the four lattice points. The junctions along the *a* direction are across hydrogen atoms. The large number of orders of (0 0 1) planes reflecting indicates a concentration of the atoms in the (0 0 1) planes. The model shows this, and also explains the very complete cleavage parallel to this plane. The other cleavage (1 0 1) is likely from the model.

Summary

m-Iodobenzoic acid belongs to the monoclinic prismatic class instead of monoclinic sphenoidal. Its axial ratio is $a : b : c = 1.3252 : 1 : 5.5824$; $\beta = 91° 29.5'$. The unit cell contains four molecules and has the following dimensions: $a_0 = 6.206$ Å.; $b_0 = 4.683$ Å.; $c_0 = 26.14$ Å. The space-group is C_{2h}^5. The molecules are located within the cell at the positions (0 0 0), ($^1/_2$ v $^1/_2$), (u $^1/_2$ w), ($u + {^1/_2}$, $v + {^1/_2}$, $w + {^1/_2}$), where u and w are approximately equal to 0, and v equals very nearly $^4/_{10}$. Model molecules, built up of wooden balls, embodying the "puckered" benzene ring fit into the cell defined above very well. The model accounts for the cleavage of the crystal.

An addition to Laue photograph technique through the use of filters has been described.

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

THE MEASUREMENT OF THE HYDROGEN-ION CONCENTRATION IN UNBUFFERED SOLUTIONS. I. THE ADSORBENT PROPERTIES OF PLATINIZED PLATINUM

BY I. M. KOLTHOFF AND TOHRU KAMEDA

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It is a well-known fact that the measurement of the hydrogen-ion concentration in a solution with an extremely small buffer capacity is a very hard problem. If a platinized electrode is used, it takes a long time before the potential is constant and it is hardly possible to find reproducible results; moreover, it is doubtful whether the final reading of the electromotive force corresponds to the PH of the original solution. It was our intention to make a careful study of the hydrolysis of solutions of pure zinc salts and we used a platinized platinum spiral for the measurement of the *P*H.[1] However, we met with many difficulties; the e.m.f. measured always corresponded to *a* higher hydrogen-ion concentration than was

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[1] For electrode cell, *cf.* I. M. Kolthoff and W. Bosch, *Rec. trav. chim.*, 46, 430 (1927).

expected from the results of other methods. Moreover, in many cases we were able to show in a colorimetric way that the solution taken from the electrode cell after the treatment with hydrogen had a more acid reaction than the original liquid. Recently a similar phenomenon has been described by H. G. Denham and N. A. Morris,[2] who found that solutions of zinc sulfate and cadmium sulfate after treatment in the hydrogen electrode became more acid. They attribute this to a reduction of the bivalent metal ions to the monovalent state, $Zn^{++} + H \rightleftarrows Zn^{+} + H^{+}$. This interpretation seems very improbable. In our experiments we observed that the solution from the electrode cell after treatment with hydrogen had no reducing properties whatsoever, which shows evidently that the original metal ions had not been reduced. There was more reason to ascribe the facts observed to the adsorbent properties of the platinized platinum, the more so since A. Frumkin and A. Donde[3] in a preliminary paper showed that platinum black can adsorb alkali from a neutral salt solution in a hydrogen atmosphere. It was shown by these authors that this hydrolytic adsorption is dependent upon the kind of gas with which the platinum black was saturated. In working with 0.2 N sodium sulfate solution they found that in a hydrogen atmosphere the platinum black adsorbed alkali to a considerable extent and the solution became strongly acid. After washing the platinum with conductivity water in a hydrogen current until the reaction did not change further, they treated the same platinum black with the salt solution or water, respectively, in an oxygen atmosphere instead of hydrogen. Under these conditions alkali was liberated and its amount was approximately equivalent to the amount of acid originally found in the hydrogen atmosphere; though, as a rule, somewhat less alkali was given off than corresponded to acid which had been formed. The most probable explanation of the phenomena is that in a hydrogen atmosphere a double layer is formed around the platinum particles, the metal being negative and the layer of hydrogen ions at the liquid side forming the positive part. Cations from the solution may displace part of the hydrogen ions in the double layer, which results in an adsorption of the cation, whereas an equivalent amount of hydrogen ions goes into the solution. If the hydrogen is removed the electrode is discharged, and the ions in the double layer are transformed into molecular hydrogen which escapes and the adsorbed cations into the corresponding metal. If oxygen is passed through, the metal is oxidized to its oxide, which gives the hydroxide with water. Now it may be expected that an oxygen electrode will show just the reverse behavior of a hydrogen electrode. However, Frumkin and Donde were not able to show that a sodium sulfate solution in contact with platinum black becomes alkaline on passing

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[2] H. G. Denham and N. A. Morris, *Trans. Faraday Soc.*, **26**, 510 (1928).

[3] A. Frumkin and A. Donde, *Ber.*, **60**, 1816 (1927).

through oxygen; as a matter of fact, they always found a slightly acid reaction. It should be remembered, however, that platinum black or a platinized platinum electrode in oxygen does not behave like an ideal hydroxyl-ion electrode, because part of the platinum may be oxidized to some oxide. In this light it is worth while to mention the recent important investigations of S. W. Pennycuick,[4] who was able to prove that in the preparation of a platinum sol according to the spark method of Bredig a little of a strong acid is formed, hexahydroxyplatinic acid, $H_2Pt(OH)_6$, which is responsible for the stability of the sol. In the discussion of our results we will come back to this point.

In our preliminary experiments we tried to reproduce Frumkin and Donde's results by working with platinum black. The latter was prepared by reduction of pure chloroplatinic acid with ammonium formate; the metal was washed for several weeks with conductivity water until the conductivity of the water after the washing had not changed. The black metal powder was very heavy, and it was almost impossible to stir it up from the bottom of the cell when a strong current of hydrogen gas was passed through. Moreover, fine particles showed a tendency to coagulate in the hydrogen current; probably due to the small surface of the metal we failed in reproducing Frumkin and Donde's results, although two different preparations of platinum black have been used. Therefore we changed the experimental conditions and took a long, thin foil of platinum, 3.5 cm. long and 2.5 cm. wide, wound in a cylindrical shape. It was mounted in a pyrex glass cell. The arrangement is shown in Fig. 1.

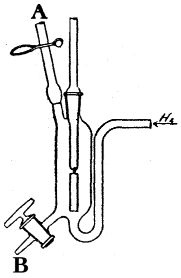

Fig. 1.

After passing the hydrogen through for a certain time, the liquid could be withdrawn from the cell in a hydrogen atmosphere by opening the glass stopcock B and closing the glass tube A. By careful electrolysis in a chloroplatinic acid-bath (without lead, of course) the platinum cylinder was coated with a black layer of platinum, then washed out with conductivity water in air and finally in hydrogen until the reaction of the water remained unchanged. The first experiments with such an electrode gave results in qualitative agreement with those of Frumkin and Donde. However, in continued investigations, a hydrolytic adsorption was no longer observed. Therefore we platinized again and washed out with sodium bicarbonate in order to remove acid which might be adsqrbed by the electrode. Thereupon the washing with water was started in the way described above but no hydrolytic adsorption was found. A third electrolysis in the chloroplatinic acid-bath was made and the electrode washed out with water in a hydrogen current until the reaction did not change further. This electrode gave continuously reproducible results, even quantitatively, and showed the adsorption phenomena quite distinctly. We do not know how to explain the first irregular behavior; we may mention here that Frumkin[5] often observed the same kind of irregularities. The hydrogen and oxygen used in these experiments were taken from a tank and purified by washing through several wash-bottles (permanganate, alkaline pyrogallol, sulfuric acid, four flasks with water, two empty wash-bottles, finally through the salt solution and then through the electrode cell). At first the hydrogen washed through perrnanganate was passed over an electrically heated copper wire; later it appeared that alkaline pyrogallol could be used as well. In the case of oxygen purification, the alkaline pyrogallol was omitted.

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[4] S. W. Pennycuiek, *J. Chem. Soc.*, **600 (1927); 551, 2108 (1928).**

[5] Private communication from Professor Frumkin.

The neutral salts used were C. P. products and were recrystallized a few times from water and tested for the absence of traces of acid or alkaline impurities.

In all the experiments conductivity water ($K_{25} = 1 \times 10^{-6}$) was used as a solvent. The qualitative experiments with solutions of sodium chloride, potassium chloride, potassium sulfate and calcium chloride showed that they became more or less acid to methyl orange when hydrogen was passed through the electrode vessel. The solutions were then withdrawn from the cell in a hydrogen atmosphere; the vessel was filled up with water or with the original salt solution, whereupon oxygen was passed through. An alkaline reaction to thymol blue and in most cases to thymolphthalein was noticed.

Before making the next experiment, the cell and electrode were washed out with water in oxygen until the reaction did not change any more. It is peculiar that after prolonged washing in oxygen the water in the electrode cell always became very slightly acid (PH 5.4 to 5.6 to methyl red sodium salt), whereas the conductivity water after washing with the same gas in a pyrex flask in the absence of platinum had a PH of about 6.8 (brom thymol blue sodium salt). Probably a trace of the hexahydroxyplatinic acid is formed in oxygen. The washing in hydrogen was followed by further washing in oxygen. In order to be sure that sulfates and salts of divalent metals (zinc) were not reduced by the hydrogen electrode, 5 cc. of the solution was transferred from the cell in a hydrogen atmosphere into 0.1 cc. of 0.001 *N* permanganate. By comparison with a blank in water we found that *no reduction of sulfates or zinc* ions had taken place. In the quantitative experiments it appeared that equilibrium in hydrogen was attained within ten minutes. The same holds for the oxygen treatment. If the latter gas is passed through for a longer time, another phenomenon may take place which we will discuss later.

As a rule 25 cc. of the salt solution to be examined was placed in the electrode cell; hydrogen was then bubbled through from ten to fifteen minutes, whereupon the solution was withdrawn into a ppex flask and titrated with 0.01 *N* sodium hydroxide, using 0.1 cc. of 0.03% methyl red sodium salt as an indicator. A blank titration was performed under the same conditions with 25 cc. of the original salt solution, washed by hydrogen. After removing the solution from the cell, the latter was filled with water in the hydrogen atmosphere, withdrawn after ten minutes and titrated. This procedure was repeated until the reaction of the wash water did not change any more. Then we continued the washing in oxygen; the water became alkaline and was titrated with 0.01 N hydrochloric acid, using methyl red sodium salt as an indicator. The procedure was repeated until the reaction of the water did not change further, whereupon the electrode finally was washed out in hydrogen again. In Table I are given only the titration figures of the first solution withdrawn from the electrode and the sum of the figures for the different wash waters.

TABLE I

0.1 *N* POTASSIUM CHLORIDE

In hydrogen	0.01 *N* NaOH, cc.	In oxygen	0.01 *N* HCl, cc.
Solution taken from cell......	0.30	First wash water............	0.32
Wash water (4 washings).....	.04	Wash water	.01
	0.34		0.33

A duplicate experiment gave in hydrogen 0.33 cc. of 0.01 *N* sodium hydroxide; in oxygen, 0.30 cc. of 0.01 *N* hydrochloric acid. There is almost a complete recovery of the base adsorbed in the hydrogen atmosphere when oxygen is passed through.

TABLE II

RESULTS OF EXPERIMENTS

In hydrogen		In oxygen	
Material	0.01 N NaOH, cc.	Material	0.01 N HCl, cc.
0.05 M Potassium Sulfate			
0.35 + 0.05 (4 washings)	0.40	0.28 + 0.04	0.32
Duplicate	.41	Duplicate	.28
0.01 *N* Sodium Chloride			
0.30 + 0.06 (4 washings)	0.36	0.30 + 0.05	0.35
Duplicate	.38	Duplicate (0.32 + 0.04)	.36
0.05 M Calcium Chloride			
0.24 + 0.04 (4 washings)	0.28	0.17 + 0.03	0.20
Duplicate	.30	Duplicate	.22

Zinc Sulfate.—More elaborate experiments were made with solutions of zinc sulfate. The salt was purified by six recrystallizations from water and dried in a desiccator over deliquescent sodium bromide at a temperature below 25°. In this way a salt with seven molecules of crystal water was obtained. After the third recrystallization, solutions of the same concentration showed the same PH.

Solutions of zinc sulfate of different strengths showed after treatment in the hydrogen electrode a much stronger acid reaction than the original ones. The usual washing in hydrogen was continued in oxygen. In the latter the reaction became only slightly alkaline, the PH being about 7 to 7.5. Even after fifteen washings the reaction was still slightly alkaline and the wash water contained a trace of dissolved zinc, as was shown by a slight opalescence on the addition of ferrocyanide. In the oxygen atmosphere the adsorbed zinc is transformed into the slightly soluble zinc oxide; it would require a long time before the latter could be washed out quantitatively. Therefore, in order to remove the adsorbed zinc, the cell was filled with 0.1 *N* hydrochloric acid and oxygen passed through from thirty to forty minutes. The acid solution contained a considerable amount of zinc; in further washing with water, no zinc was given off.

In the quantitative experiments we treated the zinc sulfate solution first in hydrogen and then withdrew the solution and titrated the free acid with m e red sodium salt as an indicator, using the original salt solution as a liquid for comparison. It was interesting to know whether an equivalent amount of zinc had disappeared from the solution. Therefore, in those cases in which we worked with 0.01 *M* zinc sulfate solution, the zinc content was determined by the oxin (o-hydroxyquinoline) method before and after the adsorption. When stronger zinc sulfate solutions were used, the difference before and after adsorption was so small that the analytical error would make the result rather uncertain. Therefore, after the zinc sulfate–hydrogen treatment, the electrode and cell were washed in hydrogen with water until the reaction remained unchanged; then we added 0.1 N hydrochloric acid, passed oxygen through and determined the amount of zinc in solution—which is equal to the amount adsorbed in a direct way by the oxin method.

TABLE III

RESULTS OF EXPERIMENTS

0.01 *M* zinc sulfate

	0.01 *N* NaOH, cc.	Adsorbed, %
In hydrogen	1.16	2.3
Adsorbed zinc	1.18	2.36

0.05 M zinc sulfate

In hydrogen: 3.03 + 0.45 (6 washings) = 3.48 cc. of 0.01 N NaOH or 0.0348 milliequiv. of H^+ liberated.
Adsorbed zinc, 0.0340 milliequiv. of Zn^{++} adsorbed

Repeated experiments gave the following results

0.0350 milliequiv. of H^+ liberated and 0.039 milliequiv. of Zn^{++} adsorbed
0.034 milliequiv. of H^+ liberated and 0.037 milliequiv. of Zn^{++} adsorbed

From these experiments we learn that the results are well reproducible, that the amount of acid formed is equivalent to the amount of zinc adsorbed by the electrode and, finally, that the adsorption of zinc ions is much larger than that of cations in alkali or earth alkali salts (compare previous tables).

Ammonium Chloride.—The behavior of ammonium chloride solution was quite different from that of the other salts. It is to be expected that the platinized electrode in a hydrogen atmosphere will adsorb ammonia. In working with 1 N, 0.1 N and 0.005 N ammonium chloride solutions, respectively, we found that in hydrogen the reaction became very slightly more acid (colorimetric measurements of P_H), the difference in acidity from the original solutions being so small that it could not be titrated (for 25 cc. of solution it was less than 0.05 cc. of 0.01 N NaOH). If the electrode was treated thereafter in an oxygen atmosphere with water after washing out, a tiny trace of alkali (ammonia) was given off.

By treating the ammonium chloride solutions in an oxygen atmosphere in the electrode cell the results were still more peculiar. The solutions became distinctly acid, more acid being formed the longer the oxygen was passed over the electrode. By passing the oxygen current coming from the electrode cell over 10 cc. of 0.004 N hydrochloric acid, we could prove in a qualitative and quantitative way that no ammonia was removed due to hydrolysis. Neither was it possible to detect in the solution after the oxygen treatment any oxidation products such as nitrate or nitrite. The only plausible explanation of the peculiar behavior was that the platinum black in the oxygen atmosphere is slowly oxidized to the hexa-aquoplatinic acid, which is very slightly soluble and remains for the main part on the electrode. This acid reacts with the ammonium ions in the solution by forming an insoluble ammonium salt

$$H_2Pt(OH)_6 + 2NH_4^+ \longrightarrow (NH_4)_2Pt(OH)_6 + 2H^+$$

The solution becomes acid and ammonium ions are removed from it. If this explanation gives a correct picture of what is happening, we may expect that after washing out with water in an oxygen atmosphere the water will become alkaline if the washing is continued in hydrogen, because the platinic acid will be reduced

$$(NH_4)_2Pt(OH)_6 + 2H_2 \longrightarrow Pt + 6H_2O + 2NH_3$$

Actually we found that the first washing with hydrogen gave an acid reaction; thereupon if the cell was filled with water again, the reaction became strongly alkaline; by means of Nessler's reagent it was very simple to detect the presence of considerable amounts of ammonia. It appears strange that the first washing in a hydrogen atmosphere gives an acid reaction. This is explained by the fact that strong acids are adsorbed by platinized platinum in an oxygen atmosphere and not in hydrogen (see later). The acid adsorbed in the oxygen treatment is rapidly displaced from the electrode by the first washing in the hydrogen atmosphere. Thereupon the reduction of the ammonium salt of the aquoplatinic acid takes place and the reaction changes to alkaline. Some of the practical results are reported in Table IV.

TABLE IV

RESULTS OF EXPERIMENTS

NH_4Cl, normality (25 cc.)		0.1	0.1	0.1	0.005	0.005
Oxygen passed for, hours		1/6	12	17	1/6	3.5
NaOH[a] for solution, cc.		0.25	1.10	1.13	0.17	0.53
NaOH[a] for washings, cc.		(4) .17	(8) 0.29	(5) 0.40	(6) 0.14	(4) 0.22
Washed in hydrogen	NaOH[a] cc., 1st.	.12	.14	.09	.04	.04
	HCl,[a] cc., 2d.	.12	.24	.32	.02	.03
	HCl[a] for more washings, cc.	(3) .12	(3) .12	(4) .16	(3) .01	(3) .03

[a] NaOH and HCl, 0.01 N.

The amount of base recovered in the hydrogen current is always much less than the amount of acid formed in oxygen. It may be that the adsorbed ammonia is not completely removed by washing out in hydrogen.

TABLE V

RESULTS OF EXPERIMENTS

Normality of $(CH_3)_3NCl$ (25 cc.)		0.1	0.1
Oxygen passed through for, hours		1/6	24
NaOH[a] for solution, cc		0 09	0.70
NaOH for first wash water, cc		.11	.10
NaOH[a] for later washings, cc		(3) .06	(3) .06
Washing in hydrogen	NaOH[a] for first.	.22	.49
	NaOH[a] for later	(5) .06	(4) .19
Washed in oxygen again	First.	No change	.09 HCl[a]
	Later (3).	No change	(3) .02 HCl[a]

[a] NaOH and HCl, 0.01 N.

We also made some experiments with the salt of an organic cation, trimethylammonium chloride. Qualitatively it behaved more or less in the same way as ammonium chloride, the only difference being that after treatment in oxygen and washing with the same gas, much more acid was liberated later in hydrogen than in the case of ammonium chloride.

Experiments similar to those described for ammonium chloride were made with 0.1 N potassium chloride. After passing oxygen through for twenty-five hours, the solution was very slightly acid and took 0.03 cc. of 0.01 *N* sodium hydroxide. The wash water (five times) took 0.06 cc. 0.01 N sodium hydroxide. Then the washing was continued in hydrogen. The first wash water was distinctly acid and took 0.06 cc. of 0.01 N sodium hydroxide; the second wash water, 0.12 cc. With four more washings the reaction did not change further. Thereupon we turned back to the washing in oxygen. The first wash water was distinctly alkaline, and took 0.05 cc. of 0.01 N hydrochloric acid and the second wash water, 0.02 cc.; by further washing the reaction remained unchanged,

These results, which are reproducible from a qualitative point of view, show that the behavior of the salt solution in oxygen is fairly complicated. After passing oxygen through for twenty-five hours, the reaction is distinctly acid, due to the formation of hexa-aquoplatinic acid. Moreover, it seems that a trace of free acid is hydrolytically adsorbed from the salt solution and that a trace of potassium is adsorbed by the platinic acid. The adsorbed acid is not given off in an oxygen atmosphere but is easily removed in hydrogen (see next section).

Therefore, the first washings with hydrogen were distinctly acid. Moreover, the hydrogen reduces the aquoplatinic acid and its potassium salt; in the latter case potassium hydroxide is formed. However, as we shall see later, a trace of adsorbed hydroxide cannot be removed in a hydrogen atmosphere but is given off in oxygen. Therefore, in the final washing in oxygen we found a slightly alkaline reaction.

On account of the complex nature of the phenomena described, it is evident that they are of no significance from a quantitative point of view.

Adsorption of Hydrochloric Acid by Platinized Platinum.—After the electrode had been carefully washed out with water in hydrogen, oxygen and hydrogen, the adsorption of hydrochloric acid was studied in a hydrogen atmosphere.

We worked with 0.01 N, 0.002 *N*, 0.001 N and 0.0005 N hydrochloric acid, respectively; the results showed that there *was not even a trace of acid adsorption in a hydrogen atmosphere.* Similar experiments were performed in an oxygen current. The oxygen was passed through for ten minutes; a longer treatment had no effect on the results. The titrations were made with 0.01 *N* sodium hydroxide using a micro buret for the more dilute solutions and methyl red as indicator. The original solutions of the acid were treated for ten minutes with oxygen in the absence of platinum black and titrated in the same way. The difference between the two titration figures gave the amount of acid adsorbed by the platinized platinum in the oxygen atmosphere. In order to be certain that there was an equivalent adsorption of the hydrogen and chlorine ions, the concentration of the latter was determined before and after the adsorption in a gravimetric way. The results agreed very closely with those obtained by the volumetric determination of the hydrogen ions. Therefore, from our experiments, we may conclude that there is *an equivalent adsorption of hydrogen and chloride ions from hydrochloric acid solution by platinized platinum in an oxygen atmosphere.* The results are summarized in the following table. In all cases 35 cc. of the acid solution was used for each experiment. The first line gives the original concentration of the acid, the second the concentration after the adsorption, the third the number of micromoles adsorbed and the fourth the decrease of the concentration of the acid due to the adsorption expressed in per cent.

TABLE VI

ADSORPTION OF HYDROCHLORIC ACID BY PLATINIZED PLATINUM IN OXYGEN

Init. concn., N	Final concn., N	Micromoles of HCl adsorbed	Adsorption, %
0.00978	0.00946	10.2	3.2
	.00951	9.5	2.7
	.00950	9.7	2.8
.00490	.00468	7.7	4.4
.00092	.00081	3.9	12
.00050	.00039	3.7	22

The curve in Fig. 2 gives a graphical representation of the change of the adsorption with the final concentration in the solution. The absolute amount of adsorbed acid increases with increasing final concentration, whereas, relatively, the adsorption decreases at higher concentrations. Therefore, the adsorption isotherm has the normal appearance. A longer treatment in oxygen did not affect the results.

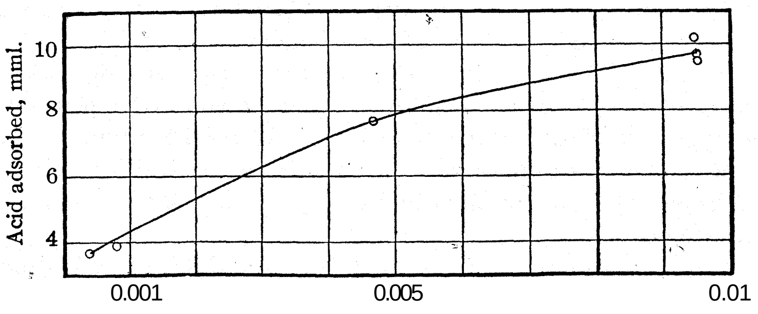


Fig. 2.—Adsorption of hydrochloric acid by platinized platinum in oxygen.

Adsorption of Sodium Hydroxide by Platinized Platinum.—As we have seen before, platinized platinum adsorbs the base from a neutral salt solution in a hydrogen atmosphere. Therefore, we may expect a much larger effect if dilute solutions of sodium hydroxide are in contact with platinized platinum in a hydrogen atmosphere. This is actually the case, though the amount adsorbed reaches a maximum at a fairly low alkali concentration; if the latter is increased, the amount adsorbed drops again. Thirty-five cc. of the solution was introduced into the cell and then hydrogen passed through for ten minutes (a longer treatment in this gas did not change the results). The solution was withdrawn in the hydrogen atmosphere and 25 cc. was titrated. The cell was washed with water in hydrogen until the reaction remained unchanged. Thereafter the washing was continued in oxygen; the wash water always was distinctly alkaline and in most cases the alkalinity was determined quantitatively. This phenomenon shows that it is impossible to remove all of the adsorbed base from the electrode in a hydrogen current. After the washing in oxygen, it was repeated again in hydrogen. In several cases we started with 20 cc. of the sodium hydroxide solution instead of with 35 cc. and analyzed later a 10-cc. portion. In the latter case only half of the electrode was covered by the solution. The titrations were made at boiling temperature with phenol red as an indicator. The original solutions have been analyzed under similar conditions. From the difference between the titration figures the amount of base adsorbed could be computed. All the results were reproducible and are summarized in Table VII.

TABLE VII

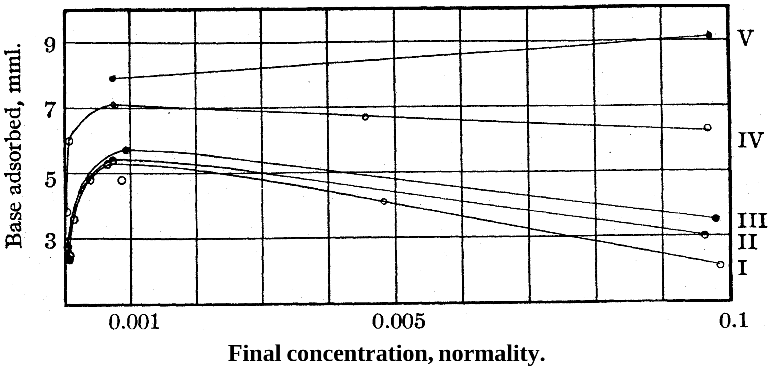
ADSORPTION OF SODIUM HYDROXIDE BY PLATINIZED PLATINUM IN HYDROGEN

Init. concn., *N*	Vol. of base taken, cc.	Final concn., *N*	Adsorbed, micromoles
0.00992	35	0.00986	2.1
.00978	20	.00963	3.0
.0049	35	.00482	4.1
.0010	35	.00086	4.8
.0010	20	.00072	5.4
.0008	35	.00066	5.3
.0005	35	.00037	4.8
.0002	35	.00011	3.6
		.00012	3.4
,00012	35	.00005	2.5
.00017	20	.00002	2.7

In Fig. 3 the results are combined in a graph; the ordinate gives the number of micromoles adsorbed and the abscissa the final concentration in the solution. It is quite evident that there is a maximum in the adsorption at a final concentration of approximately 0.0007 N sodium hydroxide. It should be remembered that a very small analytical error in the titration of the stronger solutions causes a large deviation in the amount adsorbed. Still, we believe that the general shape of the curve is right, because the values have been reproduced several times.

The shape of the curve looks similar to that representing the change of the electrokinetic potential of a platinum sol at different alkalinities. It seems to us, however, that there is no connection between the adsorption of the sodium hydroxide by platinized platinum in hydrogen and the electrokinetic potential, and it is hard at the present time to explain the maximum.

It was thought that the adsorption of the sodium ions might be increased if a sodium salt such as sodium chloride was added to the sodium hydroxide solution. This, indeed, was the case; the force required to remove the sodium ions from the solution in the presence of an excess of sodium salt is smaller than when they are absent. Under these conditions we have, moreover, the advantage that the adsorption of the hydroxide at different concentrations takes place at about the same sodium-ion concentration in the solution.



I, NaOH (35 cc.); II, NaOH (20 cc.); III, NaOH in 0.1 N NaCl; IV, NaOH in 1.0 N NaCl; V, NaOH in 3.0 N NaCl.

Fig. 3.—Adsorption of sodium hydroxide by platinized platinum in hydrogen.

The analytical procedure was the same as that described for the solutions of sodium hydroxide alone. In all cases we started with 35 cc. of solution. The results are summarized in Table VIII and graphically in Fig. 3; Curve III represents the adsorption from 0.1 N sodium chloride Curve IV from 1 *N* sodium chloride and Curve V from 3 N sodium chloride.

At larger concentrations of sodium chloride there is a decided increase in the adsorption of sodium hydroxide. Moreover, the maximum in the adsorption, which had been found at about 0.0007 N hydroxide in the absence of salt, disappears when enough sodium chloride is present.

Adsorption of Sodium Hydroxide by Platinized Platinum in Oxygen.—If a sodium hydroxide solution is in contact with platinized platinum in an oxygen atmosphere, an apparent adsorption of the base takes place.

TABLE VIII

ADSORPTION OF SODIUM HYDROXIDE IN THE PRESENCE OF SODIUM CHLORIDE BY PLATINIZED PLATINUM IN A HYDROGEN ATMOSPHERE

Concn. of NaCl, *N*	Init. concn. of base, *N*	Final concn. of base, *N*	Micromoles adsorbed
0.1	0.0099	0.0098	3.5
.1	.00097	.00080	5.7
.1	.00011	.0000	2.4
1	.0099	.0097	6.3
1	.00475	.00456	6.7
1	.00095	.00075	7.1
1	.00022	.00005	6.0
1	.00013	.00001	3.8
3	.00998	.00972	9.1
3	.00097	.00074	7.9

However, this is not a true adsorption, the amount of base which disappears from the solution increases the longer the oxygen is passed through. Some figures are shown in Table IX.

TABLE IX

APPARENT ADSORPTION OF SODIUM HYDROXIDE BY PLATINIZED PLATINUM IN OXYGEN

Concn. of base, *N*	0.01	0.001	0.001	0.001	0.0001
Passage of oxygen, hours	$^1/_6$	$^1/_6$	3.5	24	$^1/_6$
Mml. of base removed from soln.	2.8	1.8	3.2	4.4	0.36

This abnormal behavior can be explained by a reaction between the platinum black and the oxygen. The strong hexa-aquoplatinic acid is formed, which neutralizes part of the sodium hydroxide in the solution. The longer the oxygen is passed through, the more of the platinic acid is formed and the more base is neutralized. That this interpretation is right could be proved in the following way: 0.001 N sodium hydroxide was treated for twenty-four hours with oxygen in the presence of the platinized platinum. The solution was withdrawn and the vessel washed out twice with water in an oxygen atmosphere. The last wash water was practically neutral. Then water was added again and hydrogen passed through, whereupon the reaction did not change; at least the wash water required less than 0.02 cc. of 0.01 N hydrochloric acid with methyl red as an indicator. After two washings in hydrogen we turned back to oxygen. The first wash water was distinctly alkaline and took 0.11 cc. of 0.01 N hydrochloric acid; the second portion, 0.03 cc. .Continued alternate washings in oxygen and hydrogen did not change the reaction of the water. The phenomena described are well reproducible from a qualitative point of view. The sodium salt of the hexahydroxyplatinic acid which was formed in the oxygen atmosphere and adsorbed by the platinized platinum is reduced to metallic platinum and sodium hydroxide in a hydrogen gas current but, as we have seen, the platinized platinum adsorbs a trace of base in a hydrogen atmosphere very strongly. In order to liberate the base formed, oxygen has to be passed through again. It is hard to say whether the formation of the hexahydroxyplatinic acid is the only factor responsible for the disappearance of the hydroxide from the solution. It is still possible that part of the hydroxide is removed by some kind of an adsorption process.

Summary

1. The irregularities observed in the measurement of PH of unbuffered solutions with the hydrogen electrode, using platinized platinum as an electrode, are probably due to adsorption phenomena.

2. Frumkin and Donde's experiments with neutral salts in contact with platinum black were repeated with a platinized electrode. It was confirmed that platinized platinum in a hydrogen atmosphere adsorbs the cation from a neutral salt solution and an equivalent amount of free acid is found in the solution.

3. Hydrochloric acid is not adsorbed by platinized platinum in a hydrogen atmosphere, whereas a small but distinct adsorption takes place in oxygen.

4. Sodium hydroxide is strongly adsorbed by platinized platinum in a hydrogen atmosphere; a maximum occurs at a final concentration of about 0.0007 N. Sodium chloride increases the adsorption, whereas in the presence of large amounts of this salt the maximum disappears.

5. Sodium hydroxide is apparently adsorbed by platinized platinum in an oxygen atmosphere. This, however, is not true adsorption, but probably a neutralization of sodium hydroxide by the hexahydroxyplatinic acid which is formed by the action of oxygen on the platinized platinum.

6. On the same basis the abnormal behavior of ammonium chloride solutions in contact with platinized platinum in an oxygen atmosphere has been explained.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF REED COLLEGE]

A STUDY OF THE SILVER CHLORIDE ELECTRODE

BY WALTER R. CARMODY

RECEIVED APRIL 25, 1929 PUBLISHED OCTOBER 5, 1929

Although the silver chloride electrode in various forms has been used for a good many years as a reference electrode, authors have reached no agreement as to the best method of preparing this electrode. Various investigators using different methods of preparation and manipulation have obtained different results and to a certain degree the potential of the silver chloride electrode still remains in doubt, the separate electrodes varying from 0.1 mv. to as much as 1.0 mv. It was the writer's object to study the factors which cause these relatively large differences in potential in an effort to produce an electrode that would be reproducible and constant within 0.01 mv.

The silver chloride electrode has been prepared most often by electrolytically depositing silver upon platinum gauze from a cyanide solution. After being washed for a day in water the electrode is covered with a layer of silver chloride by electrolysis as the anode in dilute hydrochloric acid solution.[1] Electrodes prepared according to the directions of MacInnes and Parker have been used by several investigators,[2] and have been discarded by others[3] as being not reproducible or constant in potential. The writer selected this form of electrode for study to determine whether a constant and reproducible silver chloride electrode could be produced by this method of preparation.

Factors that Influence the Potential of the **Electrode.**—The factors involved in the preparation and use of the silver chloride electrode that influence the potential are: (1) cyanide ion absorbed in the silver-plated electrode, (2) light, (3) time and (4) concentration of chloride solution. The writer has investigated these factors in the desire to determine acceptable methods of preparation and of use of the silver chloride electrode.

The directions of MacInnes and Parker[1b] produce electrodes of "reddish-brown color the shade of which was the same whether the electrolysis was carried out in the light or in complete darkness." Noyes and Ellis[4] prepared silver chloride electrodes that were, they state, "not appreciably affected" by the action of daylight. Several years ago the writer noted

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[1] (a) Jahn, *Z. physik. Chem.*, **33,** 545 (1900); (b) MacInnes and Parker, THIS JOURNAL, **37,** 1445 (1915).

[2] (a) Harned and Brumbaugh, *ibid.*, 44, 2729 (1922); (b) Harned and Fleysher, *ibid.*, **47,** 82 (1925); (c) Scatchard, *ibid.*, **47,** 641 (1925); (d) Harned and Swindells, *ibid.*, **48,** 126 (1926); (e) Nonhebel *Phil. Mag.*, [7] *2,* 1085 (1926).

[3] (a) Lewis, Brighton and Sebastian, THIS JOURNAL, **39,** 2245 (1917); (b) Güntelberg, *Z. Electrochem.*, **17,** 179 (1911); (c) Randall and Young, THIS JOURNAL, 50, 989 (1928).

[4] Noyes and Ellis, *ibid.*, **39,** 2532 (1917).

that the odor of cyanide remained with the silvered electrodes after a period of five or six days of washing,[5] and that the shade of the color of electrodes that had been washed for two weeks did vary according as the deposition of the silver chloride was made in darkness or in daylight. Güntelberg[6] protected his electrodes from contact with light but does not mention the effect, light had upon them.

The writer prepared his silver chloride electrodes in complete darkness and protected them from exposure to light while they were being used. Results from the experimental work outlined below show that an electrolytically deposited silver–silver chloride electrode, reproducible and constant to within **0.01** mv., can be prepared if precautions are taken to protect the electrode during its preparation and use from being affected by those factors which change its potential. Both the absorption of cyanide in the silvered electrode and the exposure of the silver chloride electrode to daylight have been found to alter the potential of the electrode appreciably in the positive direction. The effect of cyanide absorption may be eliminated by washing the silvered electrode over a period of two weeks. The absorption, which determines the time of washing necessary, may be decreased by depositing the silver in an H-cell from a solution of $KAg(CN)_2$ that has been purified by careful recrystallization. The effect of daylight is eliminated by working in a dark room or by the light from an incandescent lamp, or by covering the cell with opaque cloth.

The writer has had occasion to use about fifty of these silver chloride electrodes prepared according to the directions given later in this paper. They have been found to be quite as reproducible and constant as the platinized platinum–hydrogen electrode.

Experimental

To test the effect of the time of washing of the silvered electrodes, several series of electrodes were prepared according to the directions of MacInnes and Parker[1b] in which the time of washing was varied from one to twenty days. The color and potential of the resulting electrode gradually changed until about the fourteenth day of washing, after which the silver chloride electrode produced was pure white and constant in potential. Electrodes chloridized after twenty-four hours of washing, were red-brown in color and, although checking very well within each series, were usually about **0.2** mv. positive to the white silver chloride electrodes. An attempt was made to lessen materially the time required for washing by boiling the electrodes for several hours in water and in dilute hydrochloric acid. These methods did not lessen the time appreciably.

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[5] Carmody, "Dissertation," Catholic University of America, 1926.

[6] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

The darkening of the electrodes which had not been sufficiently washed is due evidently to the reduction of the silver chloride by the traces of cyanide that are absorbed during electrolysis. In order to decrease the possibility of this absorption of the cyanide ion, the electro-deposition of the silver was carried on in an H-cell in which the two compartments were connected by a long tube, an arrangement designed to prevent hydrocyanic acid, formed at the anode, from diffusing into the cathode chamber. Also, the time of electrolysis was shortened from twenty-four to eight hours with a corresponding increase in current from three to eight milliamperes per electrode. To further insure a low concentration of the cyanide ion, the potassium silver cyanide used in the electrolysis was precipitated from a solution free from excess potassium cyanide and recrystallized twice from distilled water. The silvered electrode carried no odor of cyanide after being washed. After being washed for two days and then coated with silver chloride it was light pink in color and reproducible and constant within 0.02 mv. When the period of washing was extended to five days the resulting electrode was white and repfoducible to well within 0.01 mv.

Several series of white electrodes were prepared and subjected to the action of daylight and the light from an incandescent lamp. All became brown in color, the shade increasing with the time of exposure, and becoming positive to the control electrodes. The results are shown in Table I.

TABLE I

RESULTS OF EXPERIMENTS

Kind of light	Diffused daylight	Direct sunlight	Incandescent lamp
Time of exposure	1 minute	1 minute	12 hours
Average change, mv.	0.05	0.2	0.01

As would be expected, daylight has a much greater effect upon the potential and color than has the light from the incandescent lamp.

To determine the effect of the concentration of the electrolytic solution, two groups of silver chloride electrodes were prepared, one group in 0.1 M hydrochloric acid and the other group in 0.01 M acid. When placed in 0.1 *M* hydrochloric acid they all acquired the same potential within an hour. This demonstrates the practicability of using silver chloride electrodes in solutions of different concentration from that in which the electrodes are made. The precaution of chloridizing the silvered electrodes in a solution of the same concentration as that in which the electrode is to be used seems to be unnecessary.

The effect of time on the electrodes noted by Scatchard'' and Nonhebel and Hartley[7] was not noted. Several electrodes that had stood in distilled water for a month as well as several that had been in constant use

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[7] Nonhebel and Hartley, *Phil.* Mag., (6) *50*, 729 (1925).

in lead chloride solutions showed no difference in potential when being compared with electrodes freshly prepared. The change in potential noted by former investigators is evidently due to the action of light on the electrodes and not to any simple aging effect.

Directions for Preparing Electrodes

1. Clean platinum gauze electrodes by boiling in concentrated nitric acid for a few minutes.
2. Electrolyze as cathodes in an H-cell from a solution of potassium silver cyanide that has been prepared free from excess potassium cyanide and purified by recrystallization. The electrolysis is carried on for eight hours, *a* current of eight milliamperes per electrode being used.
3. Wash in running water for five days.
4. Electrolyze as anodes in dilute hydrochloric acid for one hour. A current density of **3** milliamperes per electrode is employed.
5. Keep in distilled water and protect from contact with direct or diffused-sunlight.

The writer is pleased to acknowledge his indebtedness to the chemistry department of Stanford University for apparatus and materials and for the privileges of their laboratory, at which the experimental work described in this paper was completed.

Summary

A study of the factors that affect the potential of the silver chloride electrode has been made.

Directions are given for its preparation and care while being used.

Results show that the electrolytically deposited silver–silver chloride electrode when carefully prepared and used is quite as reproducible and constant as the hydrogen electrode.

PORTLAND, OREGON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF REED COLLEGE]

STUDIES IN THE MEASUREMENT OF ELECTROMOTIVE FORCE IN DILUTE AQUEOUS SOLUTIONS. I. A STUDY OF THE LEAD ELECTRODE

BY WALTER R. CARMODY

RECEIVED APRIL 25, 1929 PUBLISHED OCTOBER 5, 1929

The only method of determining electrode potentials and activity coefficients from electromotive-force measurements depends upon some form of an extrapolation to infinite dilution of the experimental values obtained. This method was first outlined by Lewis and Randall.[1] Experience has shown that the curve does not flatten into a straight line necessary for extrapolation until concentrations well below **0.01** *M* are attained. Therefore, measurements on solutions of low concentration are important for the accurate determination of electrode potentials and activity coefficients.

As a general rule investigators have been unable to check one another when dealing with solutions of high dilution. A recent summary by Randall and Young[2] of the electromotive force measurements involving the silver chloride electrode illustrates the varied results obtained in dilute solutions by different investigators. The value of the normal potential of the silver chloride electrode obtained by several investigators varies from 0.2221 to 0.2234, although their measurements agree very well in the concentrated solutions.

The difficulties of electromotive force measurements in dilute solutions depend upon the relatively high percentage effect of small factors which may be negligible in the more concentrated solutions. Such slight changes in concentration may be caused by a reaction of the solution with electrodes or containing vessel or by absorption of the solution by the container or electrodes. The usual method to avoid large percentage variations due to these slight changes in concentration has been to use a cell of large proportions, containing a liter or more of solution.[3] Such cells require long periods of time, sometimes several days, to reach equilibrium. It has been the writer's experience that checks on solutions below 0.005 M are very difficult if not impossible to obtain when the large cell is used, even when the same solution and the same electrodes are used in two separate measurements.

Method and Apparatus.—The use of a small cell of 20-cc. capacity (shown in Fig. 1) designed to be emptied and refilled without the electrodes being disturbed has been

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Company, Inc., New York, 1923, p. 334.

[2] Randall and Young, THIS JOURNAL, 50, 989 (1928).

[3] (a) Linhart, *ibid.*, 41, 1175 (1919); (b) Nonhebel, *Phil. Mag.*, [7] 2, 1085 (1926).

found to yield reproducible results on solutions well below 0.001 *M*. The method of operation is as follows.

The cell, with electrodes in position, and reservoir are filled with the solution and seasoned by standing for several hours, when the solution is drawn off and the reservoir filled with a new supply. The cell is washed with this new solution from the reservoir at frequent intervals for a period of an hour or more, the time depending upon the concentration of the solution used.

After the final filling, the solution is stirred with a stream of nitrogen for a half hour. The cell is then allowed to attain equilibrium without further change of solution or stirring. After the cell has reached equilibrium and the electromotive force has been measured, a second measurement can be made readily by filling the cell with a new supply of solution from the reservoir and repeating the operation.

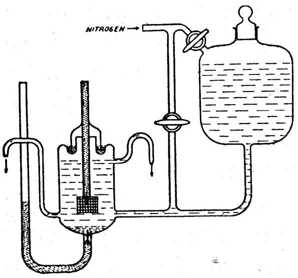

Fig. 1.

This method is designed to eliminate the effect of slight variations by using a sufficiently large volume of solution and at the same time it takes advantage of the short time necessary for the small cell to attain equilibrium. The cells described in the second half of this paper usually came to equilibrium within two hours after the nitrogen was turned off and the e.m.f. remained constant for several hours. As for the volume of the solution the writer has found it difficult to obtain checks when less than 0.001 mole of the electrolyte has been used in making up the solution. When working with concentrations approximately 0.0002 N, five liters of solution were prepared, two liters of which were passed through the cell before constant and reproducible voltages were obtained.

In the second part of this paper this method has been applied to the study of the lead electrode. A similar application of the method to the study of the silver chloride electrode in dilute solutions is planned.

The Lead Electrode

No accurate determination of the normal potential of the lead electrode has been made. Several measurements have been made that involve the potential of the lead electrode, but, since the activity coefficients of the lead salts used in these measurements are uncertain, no exact calculation of the normal potential can be made from them. Measurements of Getman,[4] Henderson and Stegeman[6] and Lewis and Brighton[6] were made on cells containing liquid junction potentials and salts of uncertain activity coefficients. Lewis and Randall[7] have roughly calculated the activity coefficient of lead chloride from the measurements of Brönsted[8] on the cell Pb, $PbCl_2$, AgCl, Ag, in which "Jahn" type silver chloride electrodes were used, by extrapolating to infinite dilution the values obtained from three measurements. Applying the activity coefficient for the saturated solution of lead chloride thus obtained to the measure-

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[4] Getman, This Journal, **38**, 792 (1916); **40**, 611 (1918).

[5] Henderson and Stegeman, *ibid.*, **40**, 84 (1918).

[6] Lewis and Brighton, *ibid.*, **39**, 1906 (1917).

[7] Lewis and Randall, ref. 1, p. 424.

[8] Bronsted, Z. *physik. Chem.*, *56*, 645 (1906).

ment of Gerke[9] on the cell Pb. $PbCl_2(s)$, $KCl + PbCl_2$, HgCl, Hg, $E = 0.5357$, they obtain the value Pb, Pb^{++}, $E_0 = 0.122$.

This value can be considered as approximate only, since it depends upon an extrapolation to infinite dilution of measurements made in relatively concentrated solutions.

Gerke also compared the potential of the two-phase saturated lead amalgam electrode with that of electrolyzed crystals and with stick lead, obtaining 0.00580 and 0.00567, respectively.

Results from the experimental work outlined below indicate that 0.0058 is a better value than 0.0057 for the potential of the lead amalgam electrode against the lead electrode. The normal electrode potential of lead is shown to be 0.1263, a value 0.0043 higher than that accepted at the present time.

Experimental

I. Electrodes and Materials

1. The silver chloride electrodes were prepared according to the method outlined by Carmody,[10] and were protected at all times from exposure to sunlight. They were prepared in groups of four, the electrodes in each group checking always within 0.02 mv.

2. The lead amalgam electrodes were prepared by heating mercury with freshly scraped stick lead (J. T. Baker's C. P.) in an atmosphere of nitrogen to form approximately a 5% solution. This was cooled to 80° and the liquid phase allowed to run into the cell through a capillary tube. The amalgam electrode so formed presented a liquid surface that was found to give more reproducible results than an amalgam that is rich in the solid phase. Repeated experiments showed it to be reproducible well within 0.01 millivolt.

3. The mercury used in the lead amalgam electrodes was purified by distilling three times in a current of air under reduced pressure as recommended by Hulett.[11]

4. Conductivity water used in preparing all solutions was the product of a laboratory still made according to the specifications given by Bengough, Stewart and Lee.[12]

5. Lead chloride (J. T. Baker's C. P.) was recrystallized three times from hot water.

6. Nitrogen for stirring cells and removing oxygen from solutions was purified by being passed in order through potassium permanganate, alkaline cuprous chloride, alkaline pyrogallol, water and finally through a solution of the same concentration as used in the cell.

II. Potential of Lead Amalgam Electrode

The Cell: Pb (Stick), $PbCl_2$, Pb(Hg).—A small cell of 20-rc. capacity was used. The freshly scraped stick electrode and the amalgam electrode were put in position in the nitrogen-filled cell. Oxygen-free lead chloride solution was allowed to run into the cell from an attached reservoir, the solution stirred with a stream of nitrogen for ten minutes and the cell then sealed. Usually the cell came to equilibrium in less than ten minutes and the potential remained constant for about two hours. After this

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[9] Gerke, THIS JOURNAL, 44, 1684 (1922).

[10] W. R. Carmody, *ibid.*, **51**, 2901 (1929).

[11] Hulett, Phys. *Rev.*, **33**, 307 (1911).

[12] Bengough, Stewart and Lee, J. *Chem. Soc.*, **131, 2156** (1927).

time a gray coating formed on the surface of the lead stick and the potential slowly lowered without again reaching a constant value.

Five different sticks (carefully selected to be free from physical defects) were used. The results, shown in Table I, are more comparable with Gerke's results from electrolyzed lead crystals than his results from lead sticks. It would appear therefore that 0.0058 is a better value for the potential than 0.0057 obtained as an average by Gerke.

TABLE I

E.M.F. VALUES OF ELECTRODES

Electrode	1	2	3	4	5	Av.
E.m.f.	0.00580	0.00585	0.00586	0.00586	0.00582	0.00584

III. The Cell: Pb(Hg), $PbCl_2$, AgCl, Ag

The electrode vessel is shown in Fig. 1. The methods of operation have already been described. Equilibrium was obtained usually within two hours after the nitrogen had been shut off. No measurement on dilutions below 0.01 M was considered until it had been checked to within 0.1 millivolt by a second reading on the same solution. Results appear in Col. 2 of Table II.

The electromotive force of the cell is given by the equation:

$$E = E_0' - \frac{0.05915}{2} \log 4\,(m\lambda)^3 \qquad (1)$$

where E_0' is the normal potential of the cell. Following the method outlined by Randall,[13] this may be transformed into the equation

$$\log \lambda - \frac{E_0'}{0.08873} = - \left[\rule{2em}{0.4pt} + 0.2007 + \log m\right] \qquad (2)$$

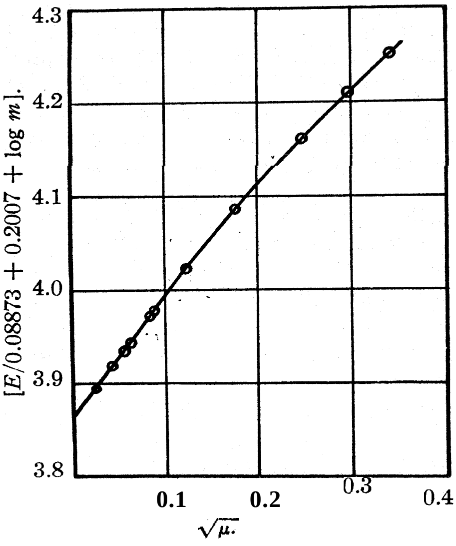

Fig. 2.

In Fig. 2 the quantity in the parenthesis is plotted against the square root of the ionic strength. By extrapolation to infinite dilution the following result is obtained: $E_0' = 0.3426$ v. Taking the potential of the silver chloride electrode to be 0.2221,[2] and the lead–lead amalgam potential to be 0.0058, the result obtained is

$$\text{Pb}, \text{Pb}^{++}, E_0 = 0.1263$$

Using this value in Equation 2, the activity coefficients of lead chloride have been calculated. They appear in Col. 3 of Table II.

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[13] Randall, *Trans. Faraday Soc.*, *23*, **498 (1927).**

TABLE II

CELL: Pb(Hg), $PbCl_2$, AgCl, Ag

M[a]	*E*, observed	λ, $PbCl_2$	M[a]	*E*, observed	λ, $PbCl_2$
0.03905	0.4842	0.408	0.002348	0.5677	0.778
.02955	.4913	.449	.001337	.5870	.830
.02048	.5012	.502	.001034	.5960	.847
.01039	.5205	.598	.0006197	.6143	.881
.005160	.5419	.692	.0002116	6537	.927
.002620	.5639	.771			

[a] The effect of the solubility of the silver chloride electrode and the hydrolysis of the lead chloride have been considered. The effects are negligible except in the most dilute solution, where they are small, approximately equal and of opposite sign.

The activity coefficient of lead chloride in saturated solution **(0.03905** *M*) is found to be **0.408.** Applying this result and the value of the potential of the calomel electrode obtained by Randall and Young[2] to the measurement of Gerke,[9] we obtain Pb, Pb^{++}, $E_0 = $ **0.1264.** This checks well with the value **0.1263** obtained by extrapolation to infinite dilution.

The writer is pleased to acknowledge his indebtedness to the Chemistry Department of Stanford University for apparatus and materials and for the privileges of their laboratory, in which the experimental work described in this paper was completed.

Summary

1. A new method of electromotive-force measurement in dilute solutions is described.
2. Electromotive-force measurements have been made on the cell Pb(Hg), $PbCl_2$, AgCl, Ag.
3. From the results of these measurements the normal electrode potential of lead and the activity coefficients of lead chloride have been calculated.

PORTLAND, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE STATE UNIVERSITY OF IOWA]

SYSTEMS FORMED BY CERTAIN TETRAHALIDES

BY P. A. BOND AND W. R. STEPHENS

RECEIVED MAY 2, 1929 PUBLISHED OCTOBER 5, 1929

Work in this Laboratory on solubilities in non-aqueous inorganic solvents has extended over several years and has included a large number of inorganic compounds. Such solvents as sulfur monochloride, liquid nitrogen tetroxide, thionyl chloride, liquid hydrogen fluoride and liquid sulfur dioxide have been investigated.[1] The work with anhydrous liquid sulfur dioxide has shown that in general the metal iodides and thiocyanates are soluble to a small degree, while the chlorides and bromides are less soluble. Bond and Beach[2] investigated the solubility of stannic chloride, stannic bromide, carbon tetrachloride and titanium tetrachloride in anhydrous liquid sulfur dioxide, and have found that these compounds form binary liquid systems at low temperatures with this solvent. They determined the nature of the systems formed by the first three of these compounds but their work with titanium tetrachloride was not completed. The present work had for its purpose the completion of the system formed by titanium tetrachloride and anhydrous liquid sulfur dioxide and the extension of the investigation to include the behavior of silicon tetrachloride and zirconium tetrachloride with this solvent.

The method employed was first used by Alexjew.[3] It consists in sealing a known quantity of solvent and solute in a small glass tube, rotating it in a bath with regulated variable temperature and noting the temperature at which the two phases become one. By doing this for a series of compositions the solubility curve may be constructed. This method offers the advantage that subsequent analyses of the saturated solutions are not necessary and the determinations are not confined to temperatures below the boiling point of sulfur dioxide. Inasmuch as solubility is practically independent of the pressure over a variation of a few atmospheres, this method is the most practical one for highly volatile solvents.

Experimental Part

The tetrachlorides of titanium, silicon and zirconium show a very great affinity for water. When exposed to moist air titanium and silicon tetrachlorides form dense white fumes, while zirconium tetrachloride gives off quantities of hydrogen chloride gas. This made it necessary to exclude as nearly as possible all moisture from the apparatus and to prevent the exposure of the compounds to the air. Another difficulty arose from the

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[1] Various unpublished theses, this Laboratory.

[2] Bond and Beach, THIS JOURNAL, 48, 348 (1926).

[3] Alexjew, *Wied.* Ann., 28, 395 (1886).

fact that titanium and silicon tetrachlorides are liquids and have considerable vapor pressures at room temperatures, which complicated transference of them to the various parts of the apparatus.

Because zirconium tetrachloride is a solid, and otherwise different from titanium and silicon tetrachlorides, it was necessary to use a different procedure for investigating it. The discussion of the experimental work with zirconium tetrachloride will, then, be taken up in the part devoted to the study of this compound.

Materials and **Procedure.**—The suifur dioxide used was the ordinary laboratory grade contained in small iron cylinders. It was purified by passing it through a train of wash bottles containing concentrated sulfuric acid and through sodium bisulfite solution. The gas was dried by passing it through calcium chloride and phosphorus pentoxide, the system consisting of tubes about one inch in diameter with a total length of thirty feet. The dried gas was condensed in a spiral condenser cooled by an ice–salt mixture and received in a special Dewar flask. This flask was so constructed as to permit withdrawal of the liquid sulfur dioxide directly from the bottom through a small outlet tube. The flask was closed with a rubber stopper. This carried a mercury seal to which the condenser was connected, another mercury seal used for the glass rod which was ground into the outlet at the bottom as a glass stopper and a third tube to permit the sulfur dioxide gas to escape. In charging the specimen tubes with liquid sulfur dioxide the rod was slightly raised and the liquid allowed to flow directly into the tubes. The total weight of mixture used varied from **2.5** to **3** g. for each determination.

Procedure.—The apparatus and the procedure in filling the tubes were the same as those described by Bond and Beach.[2] This consisted in distilling the purified material as needed into a special receiving head and admitting it to the tubes by means of a rotating flask which permitted the transference in a dry atmosphere. The tubes were attached to the outlets of the filling flask by means of cleansed rubber tubing and were connected in such a way that the tetrachloride had no contact with the rubber. After the desired amount of the tetrachloride had been admitted to the tubes, they were cooled in a freezing-bath of ice and salt before detaching them. The cooling lowered the vapor pressure of the tetrachloride and thus reduced the chance for hydrolysis, and also made it possible to seal the tubes below the boiling point of the sulfur dioxide and at atmospheric pressure. This was necessary to prevent drawing moist air into the tube when it was subsequently cooled and opened to admit the liquid sulfur dioxide. Each tube with its contents, together with the part sealed off, was weighed and from this the weight of the tetrachloride was determined. The tube was then cooled to a temperature below the boiling point of sulfur dioxide, opened by breaking off the top of the stem and the liquid sulfur dioxide admitted from the special Dewar flask. It was then sealed off as close to the liquid as possible and the mixture together with all parts of the tube weighed again. This gave the weight of the sulfur dioxide and hence the composition of the mixture.

This procedure in charging the specimen tubes provided for a minimum exposure to the air and the vaporization of the sulfur dioxide prevented to a very large degree the diffusion of water vapor into the tubes while sealing them. However, in case a trace of moisture got into the tube, its presence was shown by the ready formation of a cloudiness in the solution. Any tube showing such a condition was discarded. On account of the low temperature, and also due to the presence of sulfur dioxide gas in the tube, no measurable quantity of the tetrachloride was lost as vapor in that portion of the tube broken off.

Deterinination of Solution Temperatures.—The determination of the temperatures at which the mixtures of the various concentrations became completely miscible offered no particular difficulty for those which had solution points in the region of the binary liquid system. The solubility points in the solid–liquid region were more difficult to obtain on account of the increased viscosity of the liquids at the low temperatures and the slow rate at which the systems approached the saturation equilibrium. For those mixtures having solution temperatures above 0°, the determinations were carried out in a water-bath, the temperature of which was varied by adding small quantities of crushed ice. The temperature could be easily controlled in this manner, and any slight variation in it could be effected at will. For those mixtures having solution points at temperatures below 0° the bath consisted of acetone cooled with solid carbon dioxide and contained in a tall, unsilvered, wide-mouthed Dewar flask. The temperature in this bath could likewise easily be controlled by the rate of adding the carbon dioxide snow. As the presence of water and oil in the carbon dioxide made it undesirable for cooling at temperatures below about −50°, a eutectic mixture of acetone and chloroform **(23%** of chloroform by weight) cooled with liquid air was used instead. This latter bath remained clear and proved to be far more satisfactory for use at the lower temperatures.

In the determination of solution points the temperature was lowered until the solution showed a slight opalescence and then more slowly cooled to the point where it separated into two phases. At this point the cooling of the bath was stopped and the temperature was allowed to rise at the rate of about 1° per minute. The reading taken for the solution point in all cases was that at which the system just became homogeneous, while the temperature of the bath was slowly rising. With such a slow rate of temperature increase, together with rapid agitation of the specimen tubes, this change was sharp and the solution temperature could be read to within 0.1°.

In the region of the solid–liquid system, the solution was rapidly and sufficiently supercooled to produce crystallization whiie it was vigorously agitated. This gave fine crystals of nearly uniform size, which made the subsequent rate of solution quite uniform. The temperature of the bath was allowed to rise very slowly while the solid redissolved. Just before the last fragment of solid disappeared, the change of temperature was reversed by adding a small quantity of the cooling agent and the point at which there was any perceptible increase in the solid phase was noted. The temperature was again allowed to rise at the rate of **1** to **2**° per hour until the last fragment of crystal became almost invisible, and the temperature change was again reversed slowly to the reappearance of crystals. **A** difference between the two temperatures of **1** to **2**" for the first trials could be reduced in most cases to a difference of **0.3** to 0.4" for the last trials. The average from these latter readings was chosen as the solution temperature with a probable error of ±0.2°. In all of this work low-temperature pentane thermometers were used. These were checked against a low-temperature thermometer certified by the Bureau of Standards. In those cases where the stem could not be entirely submerged, a correction was applied and no large error could have resulted from this source.

Titanium Tetrachloride

Purification.—The starting material was an impure grade of titanium tetrachloride, colored red by ferric chloride, and containing vanadium chloride and possibly other chlorides. **A** product having a lemon-yellow color was easily obtained by fractional distillation. The yellow color was due to vanadium chloride, which has a boiling point very close to that of titanium tetrachloride, thus making further purification by"fractionation undesirable on account of the great amount of time involved. V. Merz,[4] and also M. Billy,[5] have used sodium amalgam for purifying it, and O. F. von der Pfordten[6] distilled it from sodium to remove the vanadium chloride.

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[4] Merz, *J. prakt. Chem.*, [1] *99*, **157** (1866).

[5] Billy, *Ann. chim. phys.*, [9] *16*, 5 **(1921).**

Won der Pfordten, *Ann.*, **234,257** (1886).

In this work a special fractionation apparatus combining the essential features of the apparatus described by Peters and Baker[7] and improved by Loveless[8] was used. The fractionation column was about 30 inches long and surrounded by a silvered jacket which had been evacuated. The impure beginning material was fractionally distilled from this apparatus eight times. This was equivalent to a much larger number of fractionations from the ordinary type of column. It gave a lemon-yellow product which was allowed to stand over mercury for several days and was finally distilled from mercury. The yellow color still persisted and further purification was effected by repeated distillation from metallic sodium. The sodium was carefully freed from films of oil and other carbon compounds and cut into fine shavings. It was very essential to have the sodium as free as possible from these compounds, for whenever such were present it was observed that miniature explosions, producing sparks in the flask, took place when the temperature was raised to the boiling point of the titanium tetrachloride. The liquid was digested with the sodium at an elevated temperature for about one hour before each distillation. The number of such treatments for each portion taken varied somewhat, depending on the surface of the sodium exposed and the time of digestion. In most cases as many as six or eight distillations were sufficient, the last two or three being applied after the liquid had become colorless. This gave a colorless, highly refractive product. It boiled sharply at 136.1° (752 mm. pressure), and its freezing point was −24.4°. Other observers record the following boiling points: 136.0° by Stahler,[9] 136.5° (761 mm.) by Biltz and Meinecke,[10] and 136.0° by Bond and Beach.[2] The melting point recorded by Biltz and Meinecke was −23° and that recorded by Haase was −25°.[11]

Solution Points.—The specimen tubes were filled and the solution temperatures determined as already described. The results of these determinations of the solubility points for titanium tetrachloride in liquid

TABLE I

MISCIBILITY OF TITANIUM TETRACHLORIDE WITH SULFUR DIOXIDE

$TiCl_4$, %	Soln. point	M. p., °C.	$TiCl_4$, %	Soln. point	$TiCl_4$, %	Soln. point	M. p., °C.
100.00	..	−24.4	61.80	11.9	15.02	11.2	..
98.96	..	26.0	60.46	12.0	14.44	12.2	..
97.47	..	27.7	58.40	12.0	12.26	16.8	..
96.37	..	29.1	58.05	12.0	9.53	23.7	..
96.31	−42.2	28.9	56.23	11.9	8.23	27.9	..
94.95	33.7	30.1	52.82	11.8	7.05	31.4	−31.4
90.65	13.7	..	48.20	11.5	6.44	36.1	32.7
88.66	6.3	..	43.69	11.0	4.15	..	36.1
85.35	0.3	..	37.67	9.6	3.41	..	39.3
85.16	+ 0.1	..	33.87	8.3	2.86	..	46.5
82.43	4.0	..	30.47	6.5	2.01	..	54.2
79.35	6.8	..	26.17	3.5	1.64	..	57.8
73.26	10.2	..	23.56	1.5	0.96	..	66.8
68.08	11.5	..	21.09	−1.5	...	..	..
65.40	11.8	..	19.92	3.3	...	..	..

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[7] Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

[8] Loveless, *ibid.*, **18**, 826 (1926).

[9] Stahler, *Compt. rend. trav. chim.*, *37*, 4405 (1904).

[10] Biltz and Meinecke, *Z. anorg. Chem.*, **131**, 1 (1923).

[11] Haase, *Ber.*, 26, 1053 (1893).

sulfur dioxide are contained in Table I and shown graphically in the diagram of Fig. 1. The separation of the solution into two liquid phases was sharp and the temperature at which the change took place was easily read. Opalescence near the critical solution point was slight and did not obscure the change at this temperature. In the region of the solid–liquid system the determination of the true solution points was more difficult on account of the slowness with which equilibrium developed. At concentrations below 7% and above 94.5% of titanium tetrachloride a metastable two-phase system was indicated, but it was possible to follow the binary liquid curve in this region only for a very short distance. These metastable points were obtained by slowly and carefully cooling the mixtures. In this way the solution separated into two distinct liquid phases without freezing. In every case the metastable liquid phases disappeared with rise in temperature at the same point at which the solid phase melted when frozen.

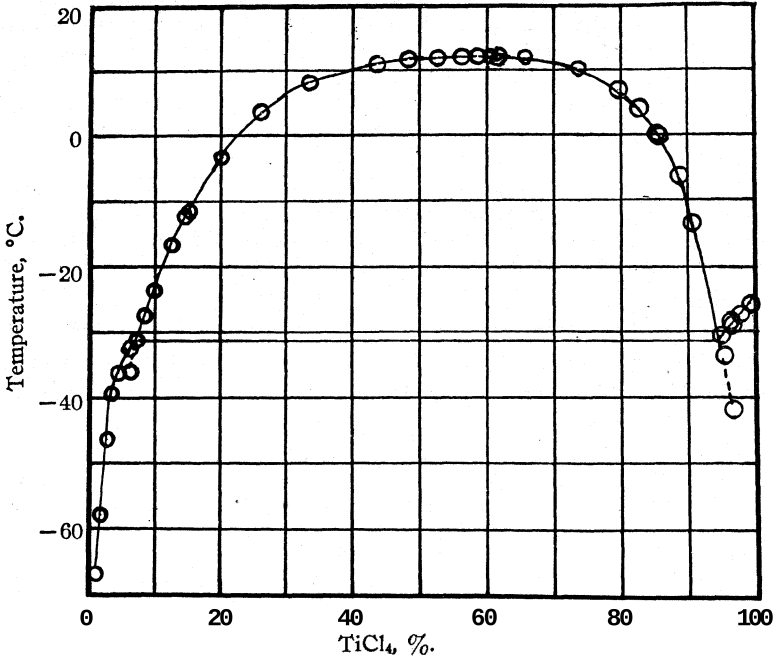

Fig. 1.—Miscibility of titanium tetrachloride with liquid sulfur dioxide.

Silicon Tetrachloride

A refined product which was colorless and appeared to be pure was taken for the starting material. It was allowed to stand over mercury for several days and finally distilled twice from mercury. It was then fractionally distilled four times, using the special fractionation apparatus already mentioned. The separation of the silicon compounds of higher order and boiling point was apparently complete by this process. The product was further distilled twice before using, the first and last portions being rejected each time. This gave a product of highest purity which boiled sharply at 56.8° (751-mm. pressure) and which had a freezing point of −69.7°. Other observers gave the following boiling points: 56.9° (760 mm.) by Becker and Meyer,[12] 56.8° (760 mm.) by Stock, Somiesky and Wintgen.[13] Latimer[14] recorded −70° for the melting point, and Stock, Somiesky, and Wintgen record −68.9°.

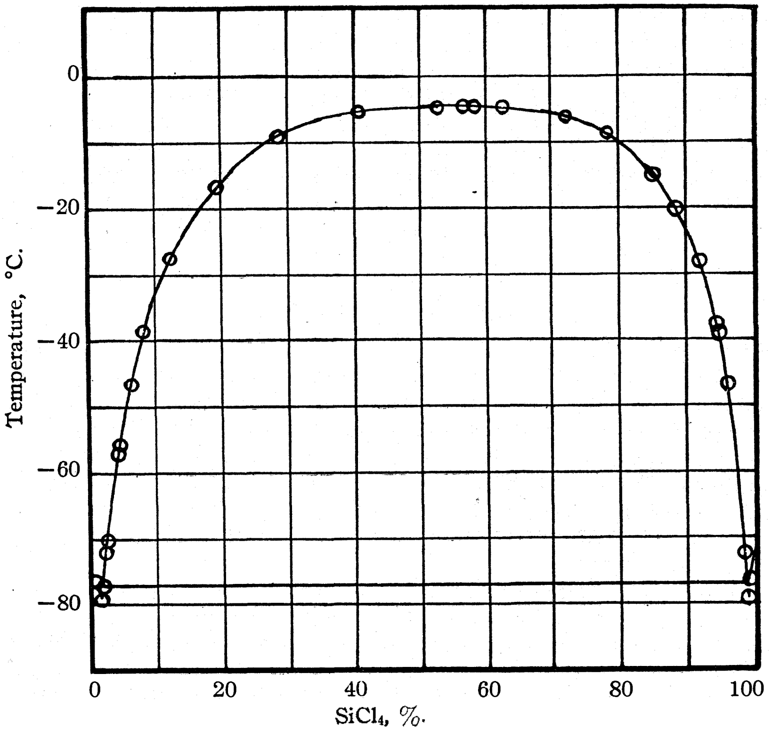

Fig. 2.—Miscibility of silicon tetrachloride with liquid sulfur dioxide.

The solution temperatures were determined in the same general way as for titanium tetrachloride. The results of these determinations are given in Table II and the accompanying diagram, Fig. 2. In the region of the binary liquid system the changes were sharp and without noticeable opalescence. In the region of the solid–liquid system the determinations were more difficult to make. The melting points were not sharp and the

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[12] Becker and Meyer, *Z. anorg. Chem.*, 43,251 (1905).

[13] Stock, Somiesky and Wintgen, Ber., 50,1754 (1917).

[14] Latimer, This Journal, 44, 90 (1922).

values given represent the average of several determinations for each mixture. The maximum error in these readings was not greater than 0.3°.

TABLE II

MISCIBILITY OF SILICON TETRACHLORIDE WITH SULFUR DIOXIDE

$SiCl_4$, %	Soln. point	M. p., °C.	$SiCl_4$, %	Soln. point	$SiCl_4$, %	Soln. point	M. p., °C.
100.00	..	−67.7	68.00	5.5	23.18	12.9	..
98.98	..	76.5	62.37	4.9	19.34	16.6	..
98.84	−77.0	79.2	60.72	4.8	15.40	22.0	..
98.70	72.4	..	58.28	4.8	12.37	27.5	..
96.03	46.9	..	56.71	4.8	10.27	32.4	..
94.66	38.6	..	54.05	4.8	8.35	38.4	..
94.37	37.5	..	52.55	4.9	6.33	46.6	..
91.90	28.2	..	46.87	5.0	4.69	55.7	..
88.46	20.1	..	45.29	5.1	4.36	57.0	..
85.19	15.0	.	40.85	5.4	2.83	70.2	..
83.12	12.8	..	37.44	6.1	2.58	72.1	..
78.19	8.8	..	33.32	7.0	1.97	79.1	−77.0
76.81	8.2	..	30.67	8.1	1.09	..	76.5
72.07	6.3	..	28.75	9.2	...	..	..

Zirconium Tetrachloride

Purification of Materials.—A quantity of purified zirconium oxychloride was taken as the starting material. It was recrystallized twenty times from hydrochloric acid and fractionally recrystallized six times from distilled water. A solution of this product gave no indication of iron with potassium thiocyanate. To remove silica it was evaporated to dryness on a steam-bath, redissolved and filtered. This was repeated and the product finally recrystallized from hydrochloric acid. This purified product was dried and strongly ignited to drive off excess hydrogen chloride and water. The product after ignition was chiefly the oxide, ZrO_2, which was used as the source material for zirconium tetrachloride.

The carbon tetrachloride was purified by allowing it to stand over calcium chloride and then over solid sodium hydroxide. It was washed with concentrated sulfuric acid and allowed to stand over phosphorus pentoxide, from which it was distilled and fractionated twice before using.

Preparation of Zirconium Tetrachloride.—The method of preparation of zirconium tetrachloride was that used by Venable and Bell.[15] This method consisted in passing a stream of dry chlorine saturated with carbon-tetrachloride vapor over zirconium dioxide heated to about 450°. The process was carried out in an apparatus essentially the same as that used by these workers. The reaction was quantitative and required only a few hours for the preparation of 10 to 15 g. There always appeared in the first product formed a small quantity of a light brown substance, presumably ferric chloride, which could be driven along before the zirconium tetrachloride by carefully controlling the temperature. To free the product from this substance, all carbon tetrachloride vapor was swept out of the apparatus with dry chlorine and the product resublimed back and forth in the apparatus several times. The zirconium tetrachloride crystallized in clear colorless needles some of which were an inch in length. This purified product was distributed among the several small bulbs and after all of the chlorine had been

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[15] Venable and Bell, THIS JOURNAL, 39, 1598 (1917).

swept out with dry air they were sealed off. The product was analyzed for chlorine volumetrically by titrating the neutral solution with standard silver nitrate, using potassium chromate as the indicator. The results by this method showed a purity of 99.9% of $ZrCl_4$. It was analyzed for its zirconium content, using the method of Lundell and Knowles,[16] which consisted in precipitating the zirconium as the phosphate in a 20% sulfuric acid solution, igniting the precipitate to the pyrophosphate and weighing as such. Results by this method showed the equivalent of 99.8% of $ZrCl_4$.

Preliminary Test for Solubility and for a **Binary** System.—The fact that zirconium tetrachloride has a high affinity for water made it necessary to transfer it to the apparatus in a dry atmosphere. For this purpose a special air-tight transference box was prepared with a glass door in the top and one side consisting of a rubber diaphragm into which rubber gloves were fixed. The rubber diaphragm permitted a fairly free use of the hands in the manipulation. This box could be filled with dry air and all transferences of zirconium tetrachloride were made in it.

A mixture of zirconium tetrachloride and liquid sulfur dioxide was sealed in a small h-shaped glass tube. The saturated solution was decanted into the side arm and sealed off. This mixture was examined at temperatures up to the critical temperature of sulfur dioxide with no indication of a binary system being formed. Evaporation of the sulfur dioxide from the tube left an appreciable residue, which showed zirconium tetrachloride to be slightly soluble in liquid sulfur dioxide.

Determination of $ZrCl_4 \cdot SO_2$.—A boiling effect was observed when the sulfur dioxide and zirconium tetrachloride were mixed, which indicated liberation of heat and the probability of chemical reaction. Further investigation showed that a solvate was formed. To establish its composition, mixtures of zirconium tetrachloride and sulfur dioxide were prepared in h-tubes as before and the decanted solutions sealed off in the side tubes in the usual manner. These tubes were placed in a freezing mixture of ice and salt and a very small opening melted in the top. The open end of the tube was then connected to a T-tube through which a current of dry air was passed. The sulfur dioxide was allowed to evaporate very slowly and at temperatures never greater than $-10°$. The time required for this evaporation was about six hours. In this way the zirconium tetrachloride was allowed to separate out very slowly and any compound formed with the sulfur dioxide would involve all of the tetrachloride. When the sulfur dioxide had evaporated, the tube was alternately evacuated and filled with dry air, disconnected from the T-tube, closed with a rubber cap, wiped dry and immediately weighed It was connected to the T-tube again and immersed in boiling water for a few minutes to drive off the sulfur dioxide of solvation. The tube was allowed to cool with dry air passing over the opening, again evacuated and filled with dry air several times, removed, dried and weighed. The loss in weight represented the weight of sulfur dioxide held by the zirconium tetrachloride. The tube was opened and the residue washed out. The parts of the empty tube were washed, dried and weighed, and from this the weight of the zirconium tetrachloride was obtained. Several analyses were made which showed the residues to be only zirconium tetrachloride. The ratio of the molecular quantities of zirconium tetrachloride and sulfur dioxide calculated from these results corresponded to the formula $ZrCl_4 \cdot SO_2$. The results of these determinations are shown in Table III. This compound crystallized in water-clear plates which appeared to be quite stable at temperatures around 0° and below. It decomposed slowly at room temperature and rapidly at elevated temperatures, reverting to a white powder.

Solubility of Zirconium Tetrachloride.—There being no existing methods for the determination of solubilities in highly volatile solvents which do not require the application of corrections that are more or less uncertain, a direct method was developed

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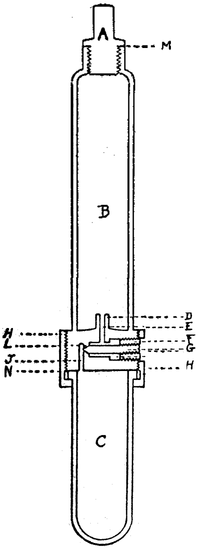
[16] Lundell and Knowles, THIS JOURNAL, 41, 1801 (1919).

Table III

Determination of $ZrCl_4 \cdot SO_2$

$ZrCl_4$, g.	SO_2, g.	Moles of $ZrCl_4$	Moles of SO_2
0.1243	0.0339	0.000533	0.000530
.1883	.0519	.000808	.000811
.1242	.0338	.000532	.000528
.0914	.0212	.000392	.000331
.1416	.0386	.000608	.000603
.2058	.0559	.000883	.000874

which is an adaptation from one previously used in this Laboratory.[17] A bomb made of monel metal was used (Fig. 3). The walls of this bomb are 1.5 mm. thick, the outside diameter of the main part is 2 cm. and the total length about 18 cm. Its weight assembled is about 210 g. It consists of two separate chambers, B and C, which are held together by the hexagonal nut H when assembled. In the lower part of B there is a needle valve arrangement which consists of the needle G, held in position by the collar F into which it screws. The needle is seated against the shoulder L, as shown, closing the outlet J. From the bottom of chamber B there is a narrow projection D 0.5 cm. long through which is a small opening to the needle-valve compartment. In order to withstand the pressure developed and at the same time to permit the manipulation of the needle, the needle valve was packed by winding rubber threads on the stem of the needle to fit into the space K. These threads when wound on G were held in place by two small washers which are not shown. The rubber was tested for the action of the solvent and of the solution on it by sealing pieces in both the solvent and in the solution, letting stand overnight, opening and examining the rubber for any change in weight or strength. No effect could be detected. Tests made to ascertain the effect of solvent or of solution on the metal of the bomb showed that if moisture was rigorously excluded no action took place.



Pig. 3.

Determination of Solubility.—The needle G was seated by grinding with 600-mesh carborundum against the shoulder L (Fig. 3). Into the opening in D was inserted a small bit of cotton to serve as a filter, and the parts were assembled as shown, using gaskets of lead foil at M and N.

The chambers B and C were washed and thoroughly dried by alternately evacuating and filling with dry air. The needle G was closed tight to shut off chamber C, and a quantity of zirconium tetrachloride transferred to B. The bomb was cooled and the liquid sulfur dioxide admitted in the usual way. The mixture was agitated in a constant temperature bath for twelve to fourteen hours. At the end of this time agitation was stopped and the bomb allowed to stand in a slightly inclined position for about an hour to permit the residue to settle to one side of D. A portion of the saturated solution in B was collected in C by loosening the needle G, and allowing it to filter into the valve chamber and to flow into C. The needle was very slightly loosened at first to prevent supercooling of the solution in the valve chamber, and any zirconium tetrachloride precipitated by the evaporation of the sulfur dioxide was deposited beyond the valve seat and subsequently swept into C by the liquid which followed.

When the sample had been thus collected, the needle was again tightened and the

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[17] Stowe, Doctor's "Thesis," this Laboratory, 1927.

bomb removed from the bath. In this way a sample of the saturated solution was collected from beneath the surface of the liquid in B. The vapor in C is therefore a part of the sample and no correction for its presence is necessary. Throughout this process the bomb was kept in a stoppered glass jacket tube to protect it from contact with the bath liquid. In the manipulation of the needle valve the bomb was raised from the bath for only a few seconds at a time.'

The excess sulfur dioxide was allowed to vaporize from B, which was then washed out with absolute alcohol and dried with ether. The bomb containing the sample was weighed. The needle G was slightly loosened and the sulfur dioxide in C allowed to vaporize in a desiccator having a current of dry air flowing through it. After the sulfur dioxide had evaporated, the bomb was alternately evacuated and filled with dry air to remove all sulfur dioxide gas from C, and was weighed to ascertain the amount of sulfur dioxide.

The bomb was disconnected and the residue in C washed out and analyzed for zirconium according to the method of Lundell and Knowles[16] already mentioned. From the previous weights and the result of the analysis of the residue, the composition of the solution was calculated. The solubility was found to be a straight-line function of the temperature; the results of determinations from 0 to 20° are given in Table IV.

TABLE IV

SOLUBILITY OF ZIRCONIUM TETRACHLORIDE

	0°		10°		20°	
Sulfur dioxide, g.......	**5.3286**	**5.2905**	**5.8132**	**6.4758**	**5.8122**	**4.1985**
$ZrCl_4$, g..............	**0.2742**	**0.2667**	**0.4247**	**0.4815**	**0.5649**	**0.4011**
Mole fraction $ZrCl_4$....	**0.0139**	**0.0137**	**0.0198**	**0.0200**	**0.0260**	**0.0257**

Discussion

The miscibility of liquids is closely connected with the polarity of their molecules. The dielectric constant gives direct evidence of polarity inasmuch as it indicates the intensity of the electrical moment in the molecule due to electron displacement. The value of this constant for titanium tetrachloride is 2.73,[18] that for silicon tetrachloride is 2.4,[19] and that for sulfur dioxide 16.2.[20] These values show titanium and silicon tetrachlorides to be alike in polarity. The greater value for sulfur dioxide could account for the partial miscibility of the tetrachlorides with it at low temperatures. Comparing the polarities of these substances on the basis of the Ramsey and Shields constant, the value of which for silicon tetrachloride is 2.20, and that given by Stowe[21] for sulfur dioxide is 2.134, we find like polarities for sulfur dioxide and silicon tetrachloride. Sufficient data were not available for calculating this value for titanium tetrachloride. To compare the polarities of these compounds further, the entropy of vaporization was calculated by applying Hildebrand's modification of Trouton's rule[22] to the value of vapor pressure at various temperatures

[18] Matthews, J. *Phys. Chem.*, **9, 641 (1905).**

[19] Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, **1924,** p. 89.

[20] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, **1924, p. 593.**

[21] Stowe, THIS JOURNAL, **51,410** (1929).

[22] Hidebrand, *ibid.*, **37,970 (1915).**

as given in the "International Critical Tables" for sulfur dioxide, and to those given by Wintgen[23] for silicon tetrachloride. This gave for sulfur dioxide the value 25.6, and for silicon tetrachloride **27.9.** Hildebrand has shown the value of this constant to be **27.4** for non-polar substances in general. The values for these compounds are in sufficient agreement with that for non-polar substances in general to indicate again their non-polarity.

Hildebrand[24] has shown that the relative internal pressures of various solvents may be estimated from the solubility data of a common solute by plotting the common logarithm of the mole fraction of the solute against the reciprocal of the absolute temperature and comparing these with a like curve for the ideal solution of the solute. The displacement of these curves from that of the ideal is a measure of their internal pressure differences, and from such a plot it is possible to arrange the solvents in a relative internal pressure series. A plot of the solubilities of liquid sulfur dioxide as the solute in the various tetrahalides as solvents was made in order to compare the relative internal pressure of these compounds. The ideal solubility curve for liquid sulfur dioxide was constructed on the basis of its heat of vaporization and boiling point. The boiling point was taken as −10° and the value of A H was that given in the Landolt and Börnstein "Tabellen" as **6157** cal. per mole. These curves are shown in Fig. 4, where the curves for carbon and stannic tetrachlorides and stannic bromide are plotted for comparison from the data given by Bond and Beach.[2] Now Stowe[21] has calculated the internal pressure of sulfur dioxide from the relation $\gamma/V^{1/3}$ to be **6.33** at 20°, where γ is the surface tension

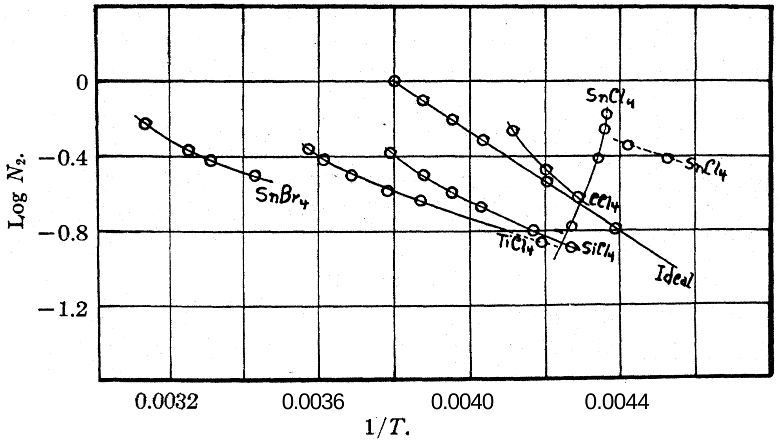

Fig. 4.—Solubility relations of sulfur dioxide.

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[23] Wintgen, *Ber.*, 52, 724 (1919).

[24] Hildebrand, ref. 19, p. 113.

and V the molal volume, and has placed liquid sulfur dioxide between chloroform and benzene in the Hildebrand solubility series.[25] Mortimer[26] pointed out that the ratio of the slope of the experimental curve to that of the ideal for any solute is a measure of the relative internal pressure of the solute and solvent. Applying this method to the curves for titanium and silicon tetrachlorides as solvents we find values which indicate titanium tetrachloride not only to belong above sulfur dioxide but also above silicon tetrachloride in the Hildebrand series. In view of this relation we would expect the miscibility of sulfur dioxide to be less in titanium tetrachloride than in silicon tetrachloride for a given temperature. The experimental results are in accord with this view.

In general this investigation has shown that the systems formed by liquid sulfur dioxide with titanium and silicon tetrachlorides accord with the principles of the various factors usually considered in the problem of solubility. The results of these measurements agree in a satisfactory way with the physical properties of the compounds, such as melting points, boiling points and dielectric constants. The critical mixing temperatures are in harmony with the various melting points and the relative positions of the elements in the periodic arrangement.

The solubility of zirconium tetrachloride in liquid sulfur dioxide was examined in the region of temperature where the compound $ZrCl_4 \cdot SO_2$ is fairly stable. The noticeable heat effect, also the formation of a solvate, when zirconium tetrachloride is mixed with sulfur dioxide would indicate a large negative deviation from Raoult's law. No data are available from which its polarity and internal pressure may be measured according to the criteria usually applied. On the basis of theory we would .expect it to have an internal pressure close to that of liquid sulfur dioxide and would also expect that its apparent higher polarity would be largely induced as a result of polar bonds within the molecule. This is in accord with the general increase of basic properties of the elements from the top toward the bottom of the periodic groups. In general the solubility relations of zirconium tetrachloride in liquid sulfur dioxide are in accord with the principles governing solubility where there is a large difference of polarity.

Summary

1. The solubility relations of titanium and silicon tetrachlorides with liquid sulfur dioxide have been determined over the entire range of compositions.

2. The solubility relations are in accord with theory as to polarity, internal pressure, melting points, etc.

[25] Hildebrand, ref. 19, p. 111.

[26] Mortimer, THIS JOURNAL, 45, 633 (1923).

3. A direct method for the determination of solubilities in highly volatile solvents has been utilized.

4. The solubility of zirconium tetrachloride in liquid-sulfur dioxide from 0 to 20° has been determined and the solvate $ZrCl_4 \cdot SO_2$ has been established.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE REACTIONS OF ETHYLENE, HYDROGEN AND THE SATURATED HYDROCARBONS UNDER THE INFLUENCE OF EXCITED MERCURY[1]

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The photosensitized combination of hydrogen and ethylene has been the subject of a number of investigations.[3] The results have been in such disagreement that it seemed worth while to reopen the subject in the hope of discovering the mechanism of what would *a priori* be considered one of the simplest of hydrocarbon reactions. This hoped-for simplicity has not been found, and no final statement as to mechanism may be ventured, but it is believed that the facts to be presented afford an empirical explanation of the variations previously found. It may also be possible, we believe, to correlate them with experiments in which the same gases, although activated by other means, react to give very similar products. We may cite, for example, the reactions of ethylene[4] in the presence of hydrogen under the influence of alpha particles. Correlation should alsa be possible with other reactions due to hydrogen atoms, which Franck and Cario[5] have shown are produced under the experimental conditions employed.

Experimental Details

Apparatus.—The apparatus used in these studies consisted of a quartz reaction vessel which surrounded the arc concentrically, thus securing as great an intensity of illumination as possible, together with a constant-volume manometer to follow the pressure changes. A gas buret and a storage reservoir were also attached through

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[1] This paper is based upon a thesis submitted by Douglas G. Hill to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Albert Plaut Fellow in Chemistry.

[3] (a) Berthelot and Gaudechon, *Compt. rend.*, 150, 1169 (1910); (b) Taylor and Marshall, *J. Phys. Chem.*, *29*, 1140 (1925); (c) Olson and Meyers, THIS JOURNAL, 48, 389 (1926); (d) 49,3131 (1927); (e) Taylor and Bates, *ibid.*, 49,2483 (1927).

[4] Lind, Bardwell and Perry, *ibid.*, 48, 1556 (1926).

[5] Franck and Cario, *Z. Physik*, 11, 162 (1922).

a three-way stopcock, and connection to the pump and to the gas analysis apparatus was made through a stopcock at the other end of the reaction vessel. Temperature control was provided by a copper water-bath in which the reaction vessel was immersed and which could be cooled by a stream of water previously brought to the desired temperature, or heated by a burner placed beneath it. A few drops of mercury were always present in the vessel, as well as in the storage reservoir, so that the gas might be saturated with mercury vapor at the temperature of the experiment.

The source of illumination was a mercury arc of the type described by Taylor,[6] constructed of pyrex glass, with a quartz section where it passed through the vessel to permit emission of the desired ultraviolet light. The base of the arc was cooled in a water-bath to 30°. This cooling is essential in order to keep the excess mercury vapor in the arc itself from absorbing the **2536.7** Å. light before it reaches the reaction vessel. An arc of this type also emits light of wave length 1869 Å., but the transmission of the quartz for this wave length is quite poor and but little could have reached the reaction system. This is indicated too by the fact that the rates were only slightly different at the end of many hundred hours of running the arc, when the quartz was quite brown. It is known that to secure transmission of 1863 Å. the quartz must be new and unusually clear. The arc was connected through a large-bore stopcock at the top to a mercury vapor pump which was kept in operation during almost all runs. It was not practicable to exhaust and seal off the arc, though this would have provided more constant conditions of intensity.

The current for the arc was supplied by a D. C. generator giving **125** volts, and resistances so adjusted that it burned at 8 amperes. The potential drop across the arc itself was about 50 volts, but due to large fluctuations in the local line voltage supplying the motor-generator, the watt load of the lamp could not be kept constant. On this account, only indirect comparison of the rates found in different experiments is possible.

The reaction vessel was exhausted by a Cenco Hyvac Oil pump capable of maintaining a vacuum of 0.001 mm. of mercury. This pressure was not attained in practice, for liquid polymers accumulated in the vessel which must have had a vapor pressure much higher than the lower limit of the pump. These would be without effect on the reaction. Air, however, was not present in the system, for unpublished experiments of Taylor and Marshall, and of Mr. A. A. Vernon in this Laboratory have shown that small quantities of oxygen added to such a reacting system cause a very large increase in rate until the oxygen is used up, when the rate drops to normal. Such an irregularity was not observed at any time in these experiments.

Preparation of Gases.—Hydrogen was taken from a cylinder, purified from oxygen by passage over hot platinized asbestos and dried by condensing the water in a trap cooled with carbon dioxide snow.

Ethylene was taken from a cylinder and dried in the same way. Analysis of the gas showed it to be better than 99% pure, with the impurity apparently higher unsaturates, which would be largely removed by the freezing mixture.

Ethane was made by catalytic combination of hydrogen and ethylene, purified as above, over nickel at room temperature. This was always accomplished in the presence of excess hydrogen, the amount being subsequently determined by analysis of the resulting mixture. For pure ethane, the hydrogen was pumped off from solid ethane at liquid air temperature, the ethane then being distilled in *vacuo* until no further gas was evolved. In most cases more hydrogen was added to the ethane as prepared to make the desired mixture for experiment.

Propane and butane were taken from cylinders and found to be upward of 98% pure. Since the impurities were other saturated hydrocarbons, they were **used** as they

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[6] Taylor, THIS JOURNAL, 48,2840 (1926).

came from the cylinders, and the whole was considered as a hydrocarbon of the average composition found by analysis.

Gas Analysis.—The gases were analyzed in a Williams gas analysis apparatus over water. Acetylene was absorbed in ammoniacal silver nitrate, saturated with ammonium nitrate to diminish the ammonia vapor pressure. Ethylene was estimated with bromine water, after which the excess bromine vapor was removed by passing the gas through a pipet which contained a strong solution of sodium thiosulfate dissolved in 33% potassium hydroxide solution. Hydrogen was determined by combustion over copper oxide at 300°, and the saturated hydrocarbons were identified by repeating the combustion on the residual gas at 500°, absorbing the carbon dioxide in potassium hydroxide solution. All the possible constituents likely to be present could be identified, though the hydrocarbons could only be given an average composition.

Experimental Results

General Considerations.—It has been observed by all the investigators who have studied the photosensitized reaction of hydrogen and ethylene that the pressure drops on illumination of mixtures containing excess hydrogen until that pressure is reached, which would be calculated, assuming that ethane was the sole product of reaction. Bates and Taylor seem to have been the first to observe that mixtures in which ethylene was the constituent present in excess must react in some other way, for the pressure drop did not stop at the theoretical point but continued at approximately the same rate. They did not follow the reaction to completion, or they would have found that the pressure change finally ceased at the pressure of the original hydrogen in this case also. This has proved to be a quite general phenomenon. In all of the mixtures of the two gases which we have used the pressure has always fallen on illumination until it reached approximately that of the hydrogen originally present, and has then remained practically constant. This change in rate is extremely sharp, dropping from 5 or 10 mm. per minute to one or two mm. per hour.

The pressure measurements alone, however, really afford no certain indication as to what the hydrocarbon may be. In a mixture of equal parts of the two gases at the start, combination to form any saturated gaseous hydrocarbon would, after the ethylene had all reacted, leave the final pressure just one-half of the initial.

Other considerations also showed that there must be other reactions taking place than the formation of ethane. For one thing, ethylene alone reacts with excited mercury, -giving first an increase and subsequently a decrease in pressure, which continues at a constant rate, but so slowly that it has never been followed to the end-point. Even with the very high light intensities used in these experiments, it would have required a number of days of illumination to bring the reaction to an end. There must therefore be at least two distinct reactions.

That there were still other possibilities was shown by the appearance of a liquid oily substance in the reaction vessel. This had been noted by previous investigators in the case in which the initial ethylene concentration was high, but our investigations show that it is formed in all cases, though most rapidly under the conditions mentioned.

Experimental Procedure I

A. The Temperature Coefficient.—In order to control the reaction as regards temperature, it was arranged to use a very rapid stream of water of the desired temperature, which should flow into the water-bath between the reaction vessel and the arc and be removed at the outside edge of the jacket. Even with as fast a stream as possible, the heat from the arc raised the temperature several degrees shortly after starting. It was necessary then to allow the arc to run with the reaction vessel evacuated until temperature equilibrium was reached, and then admit the gas as rapidly as possible from the gas buret. The pressure could be read one-half minute after the admission, and extrapolated back to the true initial pressure with sufficient accuracy. The water stream was unnecessary with runs at a temperature of 100°, where a burner beneath the vessel kept the water boiling or nearly so.

As an indication of the presence of a temperature coefficient, two experiments are given in which the temperature was varied during the course of the run, so that no other variables were introduced.

TABLE I

RESULTS OF EXPERIMENTS

	I C_2H_4, 203 mm.; H_2, 203 mm.		II C_2H_4, 395 mm.; H_2, 0 mm.			
Temp., °C.	18	40	55	23.5	100	23.5
$-\Delta p/\Delta T$, mm./min.	1.5	10.8	0.12	0.15	0.40	0.15

Discussion.—The absolute magnitudes of these temperature coefficients are not of sufficient accuracy to be of use in theoretical calculations, which will be based on later measurements, but the actuality of the temperature sensitivity is evident, and also the fact that the reaction of ethylene alone has but a very small dependence on temperature. We may therefore say that some reaction involving hydrogen is largely dependent on temperature, or is a thermal reaction, while the rate-determining process with ethylene alone is a purely photochemical one and depends on the quantity of light absorbed. This fact must be deducible from whatever mechanism is proposed.

B. Experiments with Partial Gas Analysis.—The analysis system used for the following experiments permitted the determination of the composition of the saturated hydrocarbons by combustion over copper oxide. The temperature of burning was slightly under 500°, at which point all hydrocarbons except methane burn readily. By determining the carbon dioxide formed by the combustion, the complexity of the hydrocarbons was measured and the unburned residue was considered to be methane. The results are given in Table II. The figures give pressure of the gas in mm. of mercury. Time is in minutes.

TABLE II
EXPERIMENTAL RESULTS

T. °C.	Time, min.	Total, *P*	H_2	C_2H_4	End P	C_2H	C_2H_4	H_2	Hydrocarbon	C_2H_4	$-\Delta C_2$	$-\Delta H_2$
98	30	215.5	107.7	107.7	111.5	0	0	42	46 C_2H_6	23.5	51	100
98	24	235	117.5	117.5	122.5	0	0.5	53	27 $C_{2.6}H_{7.2}$	42	60	118
100	42	482	241	241	250.5	0	2	149	66.5 $C_{3.3}H_{8\ 6}$	33	113	220
97	25	650	325	325	332	0	2.5	199	104.5 C_4H_{10}	26	100	199
53.5	45	254.5	127.3	127.3	135.5	0	1	42	42.5 $C_{2.1}H_{6.2}$	50	56	107
44	73	295	147 5	147.5	148	0	0	103	37.5 $C_{3.8}H_{9.6}$	8	70	138
53	76	409	204.5	204.5	208	0	0	119	56 $C_{3.5}H_9$	33	89	178
28	30	420	210	210	222.5	0	0	116.5	69 C_4H_{10}	37	53	95
51	70	483	241.5	241.5	245.5	0	1.5	125 5	45 $C_{5.1}H_{12.2}$	73.5	88.5	177
52.5	75	302.5	151.3	151.3	149.5	0	0	86	23 $C_{4.6}H_{11.2}$	40.5	78	157
50	91	620	310	310	317.5	0	2	144	121 $C_{3.8}H_{9.6}$	50	53	102
52	90	700	350	350	351	0	7.5	80.5	188 $C_{2.3}H_{6.6}$	75	98	192
20–100	604	395	0	395	294.5	20.5	221	2	50.5 $C_{1.5}H_5$	0	116	199

Discussion.—It will be observed that when ethylene alone is allowed to react with excited mercury, acetylene is formed. Bates and Taylor showed that both acetylene and hydrogen could be identified among the products of decomposition in the absence of initial hydrogen. Von Wartenburg and Schulze have also found acetylene but under quite different conditions, and their results will be considered later. In these experiments definite indication of acetylene was not found except in the case of ethylene alone, and the subsequent experiments show that it should only appear in mixtures initially richer in ethylene than those of Table II.

The last two columns give the amounts of carbon and hydrogen, calculated as C_2 and H_2 which have disappeared from the gas phase. This loss should be the liquid which is formed, and it will be noted that in all cases twice as much hydrogen as carbon has gone to this product.

C. The Liquid Polymer.—The liquid which is deposited in the reaction vessel during the runs is a thick, viscous oil, and difficult to remove from the vessel in quantities large enough to work with. Since the quantity formed from one hundred cubic centimeters of ethylene, which was about the average amount present during an experiment, would be very small, the oil was allowed to accumulate in a small trap over a large number of runs, and drained off by breaking a capillary *tip* when desired. By this means, of course, only the least volatile fraction was removed, for the components of low boiling point were pumped off in the course of evacuation.

Lind[7] has obtained liquid and in some cases solid substances from the

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[7] Lind, Bardwell and Perry, THIS JOURNAL, **48,** 1556 (1926); Lind and Bardwell, *ibid.,* **48,** 2335 (1926); Lind and Glockler, Trans. Am. *Electrochem. Soc.,* 52, (preprint), No. 6, September, 1927.

bombardment of ethylene and of various saturated hydrocarbons by alpha particles and has examined in detail the properties of such a liquid when produced by subjecting ethane to the silent electrical discharge. It is of interest that the polymer we have obtained by yet a third method from ethylene, and as will be shown presently from saturated hydrocarbons, agrees so closely in its properties with the substance described by Lind and Glockler. They have shown that the oil is of constant composition, close to $(CH_2)_x$ but of variable molecular weight. We have reason to believe that the oil from the photosensitized reaction is similarly constituted, since its physical properties are quite variable, but its composition as calculated from a carbon–hydrogen balance sheet is the same.

The substance, then, is a viscous, colorless, or slightly yellow oil, with an odor very reminiscent of a terpene. The mean molecular weight of a sample determined by the freezing-point depression in benzene solution was 230.

Finally, as a confirmation of the calculated composition, a sample was analyzed by combustion; 0.0308 g. of oil gave on burning 0.0393 g. of water and 0.0929 g. of carbon dioxide. A few droplets of mercury unavoidably present in the oil are responsible for the failure of the weights to correspond exactly with that of the oil. However, the calculated composition from these figures is $(C_1H_{2.07})$, which is considered satisfactory confirmation of the supposed formula.

D. The Reaction Rate.—The rate of the pressure drop seemed *so* great, as compared with all previous photochemical reactions, that experiments were conducted to compare it with a better known reaction. Taylor and Marshall[3b] showed that the pressure decrease was more rapid than that in the hydrogen-oxygen combination. Marshall[8] has subsequently investigated the latter reaction in more detail, and finds it a chain reaction, in which at least six molecules must react for each quantum of **2536.7 Å.** light absorbed. Table III gives a comparison of several experiments in the first three of which the hydrogen pressure was the same, and the other gas was respectively excess ethylene, an equivalent amount of oxygen, namely, half as much as the hydrogen, and, third, one with this same amount of ethylene. The fourth experiment contains different amounts of the gases, but in the same proportions as the first, and serves to show that the rate is fairly reproducible. All of these experiments were performed on the same day and with as nearly identical conditions as possible.

The discussion of these results will be reserved until later, for they will have more bearing on the mechanism ultimately to be proposed than in the present place.

E. Secondary Reactions.—With the same procedure as before, the possibility of secondary reactions until now unrecognized was investigated.

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[8] Marshall, *J. Phys. Chem.*, **30**, 34 (1926); 30,1078 (1926).

TABLE III

RESULTS OF EXPERIMENTS (ALL AT 100°)

P	Time	$-\Delta P/\Delta t$	P	Time	$-\Delta P/\Delta t$	P	Time	$-\Delta P/\Delta t$
H_2, 150 mm.; C_2H_4, 450 mm.			H_2, 154 mm.; O_2, 75 mm.			H_2, 100 mm.; C_2H_4, 300 mm.		
599	0	(9.5)	229	0	14	400	0	15.5
589.5	1	12.7	214	1	13.5	384.5	1	17.5
564	3	12	201.5	2	11.5	367	2	16.5
552	4	13.3	191	3	10	334	4	18.5
525.5	6	14.5	181	4	4.5	315.5	5	16.5
496.5	8	13.5	176.5	5	2	282.5	7	16.5
442	12	14.5	174.5	6	1.7	266	8	16
427.5	13	13.3	171	8	2	250	9	16.3
387.5	16		168.5	9	2.1	217.5	11	15.5
Av. $-\Delta P/\Delta t$ = 13.4 mm./min.			160	13		186.5	12	16.1
						138	16	
H_2, 152 mm.; C_2H_4, 83 mm.			Cooled to 22.5°, 61.5 = 78.5 at 100°. Therefore residue is water. Av. = (Total gas lost, calcd.)/(Total time).			Av. $-\Delta P/\Delta t$ = 16.5 mm./min.		
235.5	0	30.5						
205	1	43						
162	2	(4.5)						
157.5	3		Av. $-\Delta P/$At = 11.5 mm./min.					
Av. $-\Delta P/\Delta t$ = 36.7 mm./min.								

Several experiments were made in which a sample of the gases after illumination was removed and analyzed, and the remainder, of known composition, was re-illuminated for a further period. Analysis at the end of this time would show the later course of the reaction after the main pressure drop. The results of three typical experiments are presented in Table IV.

TABLE IV

RESULTS OF EXPERIMENTS

	T, °C.	H_2	C_2H_4	Hydrocarbon	CH_4	$-\Delta C_2$	$-\Delta H_2$
Composition at start	..	350	350	....	..	...	...
After 90 min. run	52	80.5	7.5	$188C_{2.3}H_{6.6}$	75	89	184
After withdrawing sample	..	59.2	5.1	$136.2C_{2.3}H_{6.6}$	54.3	...	...
After 60 min. more run	51	138.5	0	$48C_{3.8}H_{9.6}$	59.5	68	136
Composition at start	..	310	310	....	..	...	...
After 90 min. run	50	144	2	$121C_{3.8}H_{9.6}$	50	53	102
After withdrawing sample	..	87.1	1.2	$73.1C_{3.8}H_{9.6}$	30.2	...	...
After 30 min. more run	49	111.5	0	$38.1C_{4.3}H_{10.6}$	41.5	52	104
Composition at start	..	307.5	307.5	....	..	...	...
After overnight run	42	235	0	$3.7C_{5.5}H_{13}$	31.3	277	599

Discussion.—It is evident that very considerable reaction has occurred during the second period, for the hydrocarbons have changed both in amount and composition, while more polymer has been deposited. The remarkable fact is that the total pressure in the system has remained unchanged, or practically so, during the second stage.

Experimental Procedure II

It was necessary, therefore, to investigate these secondary reactions in a more complete manner. A number of experiments were performed on various hydrocarbons with and without hydrogen, under the same conditions of temperature and illumination as with ethylene and hydrogen.

In these experiments, the method of analysis was modified to avoid the error which was likely to result from an assumption that methane could be quantitatively separated from the other saturated gases by preferential combustion. There was no assurance that the separation was complete, and the wide variations in the relative proportions of methane and other hydrocarbons shown in Table III were an indication that methane was being burned to an undetermined extent along with the other gases.

Therefore, from this point onward in the research, the copper oxide tube was kept at a dull red heat when burning hydrocarbons, and their composition was found as an average of the entire gas. This procedure also eliminated the errors which may so readily appear in an analysis when a substance is determined solely by difference. The results of a number of runs on the hydrocarbons are given in Table V.

TABLE V

RESULTS OF RUNS ON HYDROCARBONS

T, °C.	Time, min.	Total *P*	H_2	H. C	End P	C_2H_2	C_2H_4	H_2	Hydrocarbon	$-\Delta C_2$	$-\Delta H_2$
				C_2H_6							
98	60	589.0	56.5	532.5	596.0	0	0	62.5	534 $C_{1.7}H_{5.4}$	73	147
100	60	248.0	23.8	224.0	251.0	0	0	28.5	222 $C_{1.4}H_{4.8}$	67	135
97	60	414.0	56.5	358.0	417.5	0	0	33.5	384 $C_{1.5}H_5$	71	139
100	60	399.5	70.5	329.0	395.5	0	0	82.5	313 $C_{1.95}H_{5.9}$	22	49
97	60	691.0	332.6	338.4	693.0	0	0	318.0	375 $C_{1.85}H_{5.7}$	11.5	24
97	60	686.0	341.0	345.0	691.0	0	0	324.0	367 $C_{1.7}H_{5.4}$	30	54
46	105	536.5	90.2	446.3	527.5	0	0	61.5	466 $C_{1.4}H_{4.8}$	117	242
46	120	389.5	225.0	164.5	388.5	0	0	211.0	177 $C_{1.85}H_{5.7}$	3.5	6.5
				C_2H_6 alone							
94	60	289	0	289	291.5	3	0	29.0	258 $C_{1.9}H_{5.8}$	41	79
				CaHs alone							
90	30	502.5	0	477.4 C3 25.1 C_2	509	12.5	0	81	415 C_3H_8	106	228
94	93	430.5	0	411.5 C_3 19.0 Cz	420	0	0	169	251 $C_{2.85}H_{7.7}$	277.5	566
				C_4H_{10} alone							
94	30	426.5	0	426.5 $C_{4.02}$	432	13	0	84.5	334.5 $C_{3.9}H_{9.8}$	219	405
95	180	282.0	0	282 $C_{4.02}$	280	0	0	159.0	121 $C_{3.85}H_{9.7}$	330	663
				CH_4							
97	930	575.5	386.5	189 CH_4	574.5	0	0	384	190.5 CH_4	...	
				CH_4 alone							
95	64	314	0	314 CH4	318.5	0	0	7 (?)	311 ($C_{1.3}H_{4.6}$) ?	...	...

Discussion.—The general trend is clear, though the constancy of the results is not very satisfactory. **All** the saturated hydrocarbons with the exception of methane are decomposed either by excited mercury or by hydrogen atoms, giving as final products methane, polymer and hydrogen. The small amount of reaction which the last experiment on methane and hydrogen would seem to show is ascribed to reaction of the polymer in the vessel with the hydrogen atoms. It seems quite likely that such hydrogen atoms as strike this liquid cause reaction and vaporization of small quantities of hydrocarbon. Work by Tolloczko[9] and by Bonhoeffer[10] confirms the hypothesis that methane is stable to excited mercury and to hydrogen atoms, respectively. The reason for this is not known, for from the linkage energies as commonly given, methane should react as readily as the others.

In general, then, the higher hydrocarbons react more readily than the lower. Hydrogen seems to have an inhibiting action when it is present in large quantities. Any mechanism proposed will have to take account of this fact.

Experimental Procedure 111.—In order to find which of the various reactions have ethylene as a basic material, and which depend on saturated hydrocarbons, analyses were made at different times during the reaction of hydrogen and ethylene. Mixtures of the same composition were illuminated until a predetermined pressure was reached, and then analyzed. A sufficient number of repetitions of this process gave the course of reaction until all ethylene had disappeared. A few experiments in which longer illumination was used gave the course of reaction after pressure changes had ceased. Due to the variations in intensity already mentioned, the stage of reaction could not be estimated from the time. Therefore, arbitrarily, the percentage of ethylene used was taken as a standard of reference, and the percentage figures in the table apply to that. In this way comparisons between various gas mixtures were possible. These experiments are summarized in Table VI.

TABLE VI

RESULTS WITH EXPERIMENTAL PROCEDURE III

%	T	Time. *min.*	Total P	Hz	C_2H_4	End P	C_2H_2	C_2H_4	H_2	Hydrocarbon	$-\Delta C_2$	$-\Delta H_2$
					75% C_2H_4		25% Hz					
36	100	17	410.5	102.6	307.9	333.6	13.5	195	60	65 $C_{2.9}H_{7.8}$	0	0
47	99	39	410.5	102.6	307.9	308.5	14	162	50	82.5 $C_{2.5}H_{7.0}$	28.5	41
57	100	38	412.0	103.5	309.0	273.5	16	134.5	35.5	87.5 $C_{2.9}H_{7.8}$	32	59
78	99	99	407.5	101.9	305.6	200.0	9.5	66.5	22.0	102 $C_{2.7}H_{7.4}$	94.5	179
84	98	76	410.5	102.6	307.9	179.0	10	51	18.0	100 $C_{3.1}H_{8.2}$	92	179
92	96	129	410.5	102.6	307.9	143.0	2.5	24.5	15.5	101 $C_{2.7}H_{7.4}$	147	283
95	98	113	411.0	102.8	308.2	103	0	19	21.5	62.5 $C_{2.7}H_{7.6}$	201	429.5
99	98	95	409.5	102.4	307.1	100	0	4	17	79 $C_{3.8}H_{9.6}$	153.5	313.0
100	98	347	411.0	102.8	308.2	88.5	0	2.5	45.5	40.5 $C_{1.5}H_5$	275	566
100	95	763f	410.0	102.5	307.5	94	0	0	60.5	33.5 CH_4	291	590
38	16	49	410.0	102.5	307.5	288	6.5	191	59	29.5 $C_{2.6}H_{7.2}$	71.5	164
60	15	79	410.5	102.6	307.9	190.5	2.5	121	42.5	24.5 $C_{2.4}H_{6.8}$	155	339
97	16	765	410.0	102.5	307.5	81.5	0	2.5	13.5	65.5 $C_{2.5}H_7$	223	470

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[9] Tolloczko, *Przemysl Chem.*, 2,245 (1927).

[10] Bonhoeffer *and* Harteck, *Z. physik. Chem.*, **139A,** 64 (1928).

Table VI *(Concluded)*

%	*T*	Time, min.	Total *P*	H_2	C_2H_4	End P	C_2H_4	C_2H_4	H_2	Hydrocarbon		$-\Delta C_2$	$-\Delta H_2$
62% C_2H_4 38% H_2													
41	98	5	400.5	152.2	248.3	318	14.5	146	105.5	52	C_3H_8	10	28
72	99	14	400.5	152.2	248.3	229.5	6	69	76.5	78	$C_{3.2}H_{8.4}$	48	100
98	98	13	399.5	152.0	247.5	156	0	4.5	48.5	103.5	$C_{3.2}H_{8.4}$	77.5	155
40	15	168	400	152.0	248.0	316.5	8.5	147.5	104	56.5	C_3H_8	7	15
64	16	269	400	152.0	248.0	224.5	5.5	65.5	69	84.5	$C_{3.5}H_7$	29	62
98	17	398	400.5	152.2	248.3	146.0	0	4.5	48	95.5	$C_{3.3}H_{8.6}$	89.5	190
50% C_2H_4 50% H_2													
25	96	3.5	411.5	205.7	205.7	387.5	0	153.5	189.5	24	$C_{3.7}H_{9.4}$	0	0
41	99	5.25	391.0	195.5	195.5	326	0	115.0	163.0	48	$C_{3.8}H_{9.6}$	0	0
56	100	11.5	392.0	196.0	196.0	294	0	87	145	62	$C_{3.4}H_{8.8}$	0	0
75	100	9.5	393.0	196.5	196.5	262	0	80.5	135.5	70.5	$C_{3.8}H_{9.6}$	0	0
75	100	20	392.0	196.0	196.0	245	0	43.0	123.5	78.5	$C_{3.4}H_{8.8}$	19.5	32.5
93	100	20.5	393.5	196.7	196.7	216.5	0	14	118	84.5	C_4H_{10}	13.7	21.2
98	100	20	392.0	196.0	196.0	204.5	0	4.5	110	89.5	$C_{3.8}H_{9.6}$	21.5	40.0
99	100	23	393.5	196.7	196.7	202	0	3.5	111	81.5	$C_{3.7}H_{9.4}$	32	61.5
100	53	76	409.5	204.7	204.7	208	0	0	119	89	$C_{2.5}H_7$	89	178
100	28	30	420.0	210.0	210.0	222.5	0	0	116.5	106	$C_{2.9}H_{7.8}$	53	95
37	99	9	600	300	300	500	0	188	235	77	$C_{3.1}H_{8.2}$	0	0
69	100	23	602.5	301.3	301.3	402	0	93.5	201	107	$C_{3.5}H_9$	0	0
96	100	26	599	299.5	299.5	307.5	0	11.5	158	138	$C_{3.7}H_{9.4}$	32.7	69
42	99	5.5	198	99	99	185.5	0	57.5	84	24	$C_{3.9}H_{9.8}$	0	0
72	99	11.5	199.5	99.7	99.7	134	0	27.5	69.5	39	$C_{3.8}H_{9.6}$	0	0
96	100	17	198.5	99.3	99.3	104.5	0	4.0	59.5	41	$C_{3.9}H_{9.8}$	15.3	29.3
50% C_2H_4 50% H_2													
36	15	108	401.5	200.7	200.7	334.5	0	128	162	44.5	$C_{3.7}H_{9.4}$	0	0
69	15	261	399.5	199.5	199.5	226	0	61	133.5	71	$C_{3.5}H_9$	13.5	21.7
98	15	391	402.0	201	201	202.5	0	5.5	115.5	81.5	$C_{3.7}H_{9.4}$	45	94
25% C_2H_4 75% H_2													
19	99	0.75	410	307.5	102.5	394.5	0	83.5	293	18	$C_{2.6}H_{7.2}$	0	0
27	99	1.33	410	307.5	102.5	383.5	0	74.0	287	22.5	$C_{2.7}H_{7.4}$	0	0
48	100	3	410	307.5	102.5	359.0	0	53	268	38	$C_{2.7}H_{7.4}$	0	0
73	100	6.25	411	308.3	102.7	336	0	27	252.5	56	$C_{2.7}H_{7.4}$	0	0
73	94	7	410.5	307.9	102.6	334.5	0	26.5	259	49	$C_{2.9}H_{7.8}$	5	10
98	96	7	409.5	307.1	102.4	309.5	0	2	248	60	$C_{2.8}H_{7.6}$	16.5	33
98	98	11	409.5	307.1	102.4	310.5	0	2	261.5	47	$C_{2.9}H_{7.8}$	32	64
100	98	180	409.5	307.1	102.4	310.5	0	0	280.0	28	$C_{1.8}H_{5.6}$	77	154
100	87	750	413	309.8	103.2	319	0	0	299.5	19.5	CH_4	93.5	177
37	16	49	409.5	307.1	102.4	376.5	0	65.0	287.5	24	$C_{2.6}H_{7.2}$	0	0
68	15	65	410	307.5	102.5	339.5	0	32.5	261	46	$C_{2.4}H_{6.8}$	15	30
99	16	206	410.5	307.9	102.6	310.5	0	1.5	257	52	$C_{2.7}H_{7.4}$	31	60
10% C_2H_4 90% H_2													
33	96	1.5	600.5	540.4	60.1	580.5	0	40	515.5	25	$C_{1.95}H_{5.9}$	0	0
77	97	2	600	540	60	556	0	13.5	499	42	$C_{2.05}H_{6.1}$	0	0
97	97	4.5	599.5	539.5	60	542	0	2	489	50.5	C_2H_6	7.5	15
100	98	164	599.5	539.5	60	541	0	0	517	24	CH_4	48	96
31	16	107	599	539	60	574	0	41.5	511	21.5	$C_{1.8}H_{5.6}$	0	0
74	16	167	600	540	60	553	0	15.5	491	47	$C_{1.9}H_{5.8}$	0	0
100	16	411	600	540	60	532.5	0	0	499	33.5	$C_{1.4}H_{4.8}$	36.5	81

Discussion.—It appears at once that the primary reaction of ethylene and hydrogen is the formation of saturated hydrocarbons, but not, in most circumstances, ethane. The composition of this saturated product depends on the concentration of the original mixture and is independent of the pressures used in our experiments. It is also practically independent of temperature. It may be that there is a temperature dependence which requires greater accuracy of analysis than was possible. Such a relation might be expected on the basis of the dependence of the reaction rate on temperature, which is very clearly shown.

The polymerization is a secondary reaction, and all, or at least practically all, polymer must go through the intermediate stage of saturated hydrocarbon. This is subsequently decomposed and deposits polymer, changing in composition at the same time, until nothing but methane and hydrogen is left in the gas phase.

The rate of reaction depends both on temperature and on composition of the gas. The temperature coefficient is very much greater for an initial mixture richer in hydrogen, so that this temperature dependence involves some reaction with hydrogen. All these restrictions must be satisfied by the proposed mechanism.

Mechanism of the Reactions

Taylor and Bates[3e] have proposed a mechanism for the reaction between ethylene and excited mercury which seems to be in accord with the results presented here. Their scheme of reaction between ethylene and hydrogen atoms, which reaction seems to be the more important in many cases, requires revision. The actual processes must be quite complex, so that a qualitative explanation is all that may be given. The following, then, is offered as one, possibly of many conceivable mechanisms, which will explain the observations. The reactions will be tabulated here and discussed in detail subsequently.

$$\mathrm{C_2H_4 + Hg' \longrightarrow C_2H_2 + H_2 + Hg} \qquad (1)$$

$$\mathrm{C_2H_2 + Hg' \longrightarrow Cuprene}$$

$$\mathrm{C_2H_2 + H \longrightarrow Liquid\ polymer}$$

$$\mathrm{H_2 + Hg' \longrightarrow 2H + Hg + 12{,}000\ cal.} \qquad (2)$$

$$\mathrm{H + C_2H_4 + Hz \longrightarrow C_2H_6 + H + 5000\ cal.} \qquad (3a)$$

$$\mathrm{H + C_2H_4 + C_2H_4 \longrightarrow C_2H_5 + C_2H_4 + 15{,}000\ cal.} \qquad (3b)$$

$$\mathrm{C_2H_5 + C_2H_4 + Hz \longrightarrow C_4H_{10} + H + 5000\ cal.} \qquad (4a)$$

$$\mathrm{C_2H_5 + C_2H_4 + C_2H_4 \longrightarrow C_4H_9 + C_2H_4 + 15{,}000\ cal.} \qquad (4b)$$

$$\mathrm{C_2H_5 + C_4H_9 \longrightarrow C_4H_8 + C_2H_6 + 55{,}000\ cal.} \qquad (5)$$

$$\mathrm{C_2H_6 + H \longrightarrow CH3 + CH_4 + 20{,}000\ cal.} \qquad (6)$$

$$\mathrm{C_4H_{10} + H \longrightarrow C_3H_7 + CH4 + 20{,}000\ cal.}$$

$$\mathrm{C_4H_{10} + Hg' \longrightarrow C_3H_7 + CH3 + Hg + 52{,}000\ cal.} \qquad (7)$$

$$\mathrm{C_2H_5 + C_2H_6 \longrightarrow C_4H_9 + H_2 - 10{,}000\ cal.} \qquad (8)$$

$$\mathrm{C_2H_5 + Hz \longrightarrow C_2H_6 + H - 10{,}000\ cal.} \qquad (9)$$

The reactions under (1) have been discussed by Taylor and Bates[3"] and Reaction 2 has been well established by the work of Franck and Cario,[5] so that neither need be treated here.

It is to reactions of the types indicated in (3) that we ascribe the principal course of reaction. Modern ideas, arising originally from quantum considerations, have shown that direct addition of two molecules to form one in the gas phase is an extremely improbable occurrence. For that reason we cannot assume that a hydrogen atom can add directly to an ethylene molecule to form a free ethyl radical. Such an addition can take place, however, if a third body is present at the collision, or, which amounts to the same thing, if a third molecule collides with the reactants during the short time during which an unstable pseudo-molecule might exist. If the third body is an ethylene molecule, as in (3b), it seems unlikely that anything other than the stabilization of a free ethyl radical would result. If the third body is hydrogen, however, a reaction to form ethane with liberation of a hydrogen atom is possible. This may, of course, take place in two steps, an ethyl radical being formed first, which subsequently reacts with another hydrogen as in Reaction 9, but the great rapidity of the reaction in the case where ethane is the sole product makes a mechanism of as few steps as possible the more preferable. It will be noted that (3a) has the character of a chain reaction, in that the hydrogen atom is capable of forming a large number of ethane molecules. The comparative rate measurements in Table III indicate that a chain is formed, since the rate is much faster than that of an established chain reaction.

Presumably the temperature coefficient is also to be ascribed to Reaction 3a, since the ethane is formed by this process. The results show that the temperature coefficient is greatest in the gas mixture which is transformed almost quantitatively to ethane. By inserting the temperature coefficient in this case in the Arrhenius equation, we can calculate that it corresponds to an activation energy of about 10,000 calories. In spite of this agreement, it is probably unjustifiable at the present time to connect this with the endothermic Reaction 9 and attempt to maintain the multi-stage reaction so indicated.

The reactions included in (4) are assumed to be typical of the early stages of the reaction, where ethylene is present in considerable quantities. It is possible to invent reactions which are possible energetically, almost at will. All that is necessary is that higher saturated hydrocarbons and higher radicals should result, as in (4a and 4b).

Reaction 5 is of a different type, and is the method by which the unsaturated polymer must be formed. Just what hydrocarbons are the products is unknown, and it is not improbable that Reaction 5 should form amylene and methane instead of butylene and ethane. Work of Mr. W. H. Jones in this Laboratory (to be published shortly) confirms the mechanism advanced here in so far that free radicals react to form unsaturated and saturated hydrocarbons, and that in the presence of hydrogen and ethylene, products similar to those of Reaction 4 occur.

The saturated hydrocarbons which are formed by a process such as (4a) or (5) have been shown in Table V to be decomposed both by hydrogen atoms and by excited mercury atoms. Since radicals must be formed by such reactions, we have postulated in Reactions 6 and 7 that methane or methyl and a residue are formed at once. The fact that methane is not attacked under the conditions of the reaction, but, on the contrary, is formed as a stable product in increasing quantities as exposure is continued, speaks for this hypothesis. These radicals will, as a rule, no longer react as in (4), owing to the low concentration of ethylene at the stage in the reaction where the saturated hydrocarbons are largely attacked. They will be limited primarily to Reaction 5, forming low concentrations of unsaturates which will be rapidly built up to high molecular weights as in (4b), and finally condense as liquid polymer by a repetition of (5). One would predict from this scheme that polymer, which implies high unsaturates, would be formed more rapidly after the primary ethylene was used up, for in this case the sole reaction of the hydrogen or the excited mercury is the production of the necessary radicals. This hypothesis is wholly confirmed, for Table VI shows that polymer appears late in the reaction in those cases in which reactions of the type of (3a) would predominate.

Reactions 8 and 9 are endothermic, but of small enough heat value so that their occurrence is of moderate frequency. In fact it is not unreasonable to expect that reactions of this type which can be calculated to occur on about one collision in a million will be quite appreciable, since the other possibility involves two radicals, which must be of very small concentration. Granted these reactions, then, we can explain the retarding effect on the decomposition of saturated hydrocarbons which large amounts of hydrogen appear to have.

Discussion of Other Results

The mechanism which is proposed can be shown to accord with the experimental results of other investigators.

Olson and Meyers[3] analyzed the gases resulting from the photosensitized reaction of hydrogen and ethylene by positive ray methods and found methane, propane and butane in the gas phase as well as the ethane that was expected. No mention is made of polymer formation in connection with these analyses, though they observed its formation in their earlier work.

We are not able to understand, however, the statement of these authors that ethane does not react when bombarded by excited mercury atoms. That there is no material pressure change is in accord with our findings, but the positive ray analysis should have shown a number of other hydrocarbons present and also hydrogen. This latter might have escaped notice on account of its small mass. The work of Tolloczko[9] confirms that reported here in that ethane is and methane is not attacked by excited mercury.

Bonhoeffer and Harteck[10] have recently published a paper in which they present spectroscopic evidence to show that ethylene, ethane and other hydrocarbons, except methane, are attacked by hydrogen atoms and stripped of their own hydrogen until very simple residues remain. They pulled atomic hydrogen from a discharge tube into the gas, and observed in the resulting luminescence the bands which are assigned to the C–C and the C–H radicals. We may suggest that the fact of spectral emission does not require the presence of more than a very minute quantity of the excited substance. In their experiments only slight quantities could be present, for it requires a number of collisions with hydrogen atoms to produce the radicals under any mechanism, and the nature of the method requires low pressures, where such multiple collisions will be rare.

Their results are explicable under our mechanism. It should be impossible to split an ethylene molecule into two CH_2 radicals on collision with a hydrogen atom. Fracturing a double bond demands about 125,000 calories, which the hydrogen atom cannot supply. If the primary process is that postulated here, the reaction would involve primary formation of ethane, and decomposition of that, which according to our mechanism would give both methyl and ethyl radicals. These may then lose hydrogen further, and will do so the more readily under their conditions, since the concentration of hydrogen atoms is so much greater.

Von Wartenburg and Schulze[11] have analyzed the products of reaction conducted by Bonhoeffer and Harteck's method, and find results quite compatible with our own. The saturated hydrocarbon is practically pure ethane, as it should be with the large excess of hydrogen present. In the decomposition of ethane they find but slight change in the gas. It would be but slight under their conditions and would probably have escaped notice, for the analysis depended on freezing the effluent gases. Methane and hydrogen would have passed through the liquid-air trap even if formed.

Conclusion

1. The reaction between hydrogen and ethylene under the influence of excited mercury atoms has been investigated with varying conditions of pressure, concentration and temperature. The concentration is the only factor which has any effect on the course of the reaction.

2. The reaction proceeds the more quantitatively to form saturated hydrocarbon the greater is the concentration of hydrogen. The particular hydrocarbon formed is also dependent on the composition of the original mixture illuminated. High hydrogen concentration favors mainly ethane formation.

3. These saturated hydrocarbons are subsequently decomposed both by excited mercury atoms and by atomic hydrogen, and yield methane as the stable product in the gas phase. At the same time a liquid polymer of composition C_xH_{2x} is deposited on the walls. Methane is unattacked by either excited mercury or by atomic hydrogen.

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[11] Von Wartenburg and Schulze, *Z. physik. Chem.*, [B] 2, 1 (1929).

4. A mechanism is proposed to explain these results. It can be shown to be in accord also with the results of other experimenters.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

REDUCTION REACTIONS WITH CALCIUM HYDRIDE. I. RAPID DETERMINATION OF SULFUR IN INSOLUBLE SULFATES[1]

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Almost all quantitative methods of determining sulfur in either organic or inorganic matter have as their method of procedure the oxidation of the sulfur to sulfate and subsequent precipitation with barium chloride. With reductive reactions of calcium carbide and calcium hydride in mind it was thought of interest to see whether the sulfur in various compounds, both organic and inorganic, could be quantitatively converted to calcium sulfide by ignition with these substances. If the sulfur were quantitatively changed to calcium sulfide, it could be estimated by acidifying the soluble sulfide solution, followed by iodimetric titration.

The hardest test to which this reasoning could be put was to attempt quantitative reduction of sulfates to sulfides. The amount of soluble sulfide formed was then to be determined with standard iodine solution. The present paper will report results of such experiments.

Sulfur in a steel has long been determined by heating a sample of steel filings with hydrochloric acid in a closed system, dissolving the evolved hydrogen sulfide from the sulfide in the steel in either ammoniacal cadmium chloride or caustic soda solution. The absorbing solution is then diluted with water, acidified with hydrochloric acid and titrated with iodine, using starch as indicator. Soluble sulfides such as calcium sulfide and sodium sulfide may also be determined by iodine titration.

A few investigators have studied reductions of sulfur compounds to sulfides in a quantitative way. Luigi Losana[2] has attempted to reduce sulfur to sulfide by ignition with a mixture of sodium bicarbonate and iron powder. The ignited mass was placed in an evolution flask and treated with acid much as in the determination of sulfur in steel. The method is said to be of general application for inorganic sulfur compounds.

Other metals and mixtures of metals and salts have been tried in effecting conversion of oxy-compounds of sulfur to sulfides. H. Bahr and W. van

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[1] This paper is prepared from the first part of a dissertation on reduction reactions with calcium hydride, to be presented by William E. Caldwell in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Losana, *Giorn. chim. ind. applicata,* 4, 204–206 (1922).

der Heide[3] used a mixture of barium peroxide and powdered aluminum. B. N. Tiutiunnikov[4] mixed in a heavy infusible glass tube magnesium powder, strips of magnesium ribbon and a sulfur containing substance. Some unpublished work involving sodium fusions with sulfur compounds has been carried on by a colleague.

Experimental

Sulfate Reductions with Calcium Carbide.—Calcium carbide is a more easily obtained and a cheaper compound than calcium hydride. Calcium carbide decomposes upon being heated, yielding metallic calcium and carbon, both in themselves reductive. It was desired to see how complete a reduction of sulfate could be had with powdered carbide. Ebler and co-workers[5] used mixtures of calcium hydride and calcium carbide in partially reducing sulfates in recovering radium from a sulfate mixture; 60–65% reduction is reported on spontaneous fusion.

Commercial calcium carbide is found to contain considerable sulfur, probably due to gypsum occurring with the carbonate from which the carbide is made. A purer, specially prepared carbide was obtained which analyzed 0.034% sulfur. Thus a weighed amount of carbide must be used in the fusions and a correction must be applied to all sulfur determinations. If a carbide free from sulfur were obtainable, it would eliminate a weighing and a correction.

Seven-tenths gram of the carbide was ground to 60-mesh and thoroughly mixed with 0.5 g. of potassium sulfate in a 25-cc. iron crucible. This crucible was heated over a Méker burner and the resultant fusion mass placed in an Erlenmeyer evolution flask for hydrogen sulfide evolution. The evolved hydrogen sulfide was collected in ammoniacal cadmium chloride solution, which was then acidified and titrated for sulfur content with iodine. As water and acid were added to the fusion mass in the evolution flask, acetylene was formed therefrom by action on undecomposed carbide, thus yielding a reducing atmosphere, insuring that no sulfide would be oxidized by the air in the apparatus. Results are given in Table I.

TABLE I

ONE-HALF GRAM OF POTASSIUM SULFATE REDUCED TO SULFIDE WITH CALCIUM CARBIDE

0.5 g. of K_2SO_4 = 0.0915 g. of S

Sample	I_2 titer, cc.	Sulfur equivalent, g.	Reduced S/ total S	Reduction. %
1	48.0	0.0768	0.0768/0.0915	84.0
2	48.6	.0776	.0776/0.0915	84.9
3	49.0	.0784	.0784/0.0915	85.8
4	45.0	.0720	.0720/0.0915	79.0
5	46.0	.0736	.0736/0.0915	81.0

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[3] Bahr and van der Heide, *Z. angew. Chem.*, 37, 848–851 (1924).

[4] Tiutiunnikov, Chem. *Zentr.*, II, 264 (1924).

[5] Ebler and others, Ber., 46, 2264 (1913).

Quantitative reduction was not obtained. It was attempted to increase the yield of reduced sulfur by mixing sodium carbonate with the calcium carbide, thinking to hold back any escaping sulfur dioxide. When this was done but 60% of the sulfur was reduced to sulfide.

Calcium hydride should have the following advantages over calcium carbide: first, it is more easily obtained free from sulfur; second, evolution of hydrogen sulfide is more readily carried on from hydride residues than from carbide fusion residues, as some free carbon remaining from calcium carbide fusions tends to hold back hydrogen sulfide (it was later found that evolution from calcium hydride fusions residues was unnecessary, acidification of the water solution of the fusion residue, followed by titration, being all that is needed); third, hydrides remaining in the fusion mixture decompose with water to give off hydrogen while carbides with water yield undesirable, odorous acetylene. The hydride might give more complete reduction on fusion with sulfates.

Sulfate Reductions with Calcium Hydride.—Calcium hydride may be obtained from various chemical distributors. It is a light gray solid which may be readily ground in a mortar. All of the calcium hydride used in this work was powdered by means of a small disk grinder and passed through a 60-mesh screen. The grinding must not be too rapid or the heat of friction may cause ignition of the calcium hydride.

Samples of the hydride were tested for sulfur and no trace was detected. The calcium hydride does, however, contain calcium chloride and calcium oxide. The calcium chloride probably comes from the preparation of metallic calcium from which the hydride is made. The calcium oxide is the result of the reaction of the hydride and moisture. In the procedures used neither of these impurities hinder reductive action on sulfates.

Calcium hydride acts on water thus:

$CaH_2 + 2HOH = Ca(OH)_2$	$+ 2H_2$
42 grams	4 grams or 44,800 cc.
1 gram	1,067 cc.

One gram of calcium hydride should evolve 1067 cc. of hydrogen at standard conditions. The purity of the hydride was determined by measuring the hydrogen evolved from a weighed amount. An average of runs indicated that the hydride yielded 803.4 cc. of hydrogen at standard conditions. It is readily seen that we were not dealing with pure calcium hydride but a mixture of calcium hydride, calcium oxide, calcium chloride and probably some sub-hydride of calcium.

A sample of calcium hydride was made in this Laboratory by passing hydrogen over rasped calcium, heating in a pyrex tube to about 500° in a small electric furnace. This product was a light gray, easily ground solid, comparable to that obtained on the market. It also yielded much less than the theoretical amount of hydrogen on treatment with water.

As moisture was kept from the product and since very little chloride is present, the deficiency in amount of evolved hydrogen is probably due to a sub-hydride of calcium.

Fusions for sulfur estimation were made upon purified sulfates of potassium, barium, strontium, calcium and lead. The comparisons of these results with the theoretical are listed in later tables. Carefully standardized 0.1 *N* iodine and sodium thiosulfate solutions were used in titrations.

Of the various methods of procedure that were tried for running sulfur determinations on sulfates, starting by ignition with calcium hydride, the following outlined process gave the best results.

One-half or 0.25 g. sample of the crushed sulfate were mixed in a 25-cc. iron crucible with about 7 g. of powdered calcium hydride. This amount of hydride about half fills the crucible. Mixing is accomplished with a spatula; about thirty turns of the spatula are deemed sufficient. A surface layer of hydride is placed above this mixture to the depth of one-eighth inch.

A cover is placed on the crucible and the whole quickly heated over the full blast of a Méker burner and then allowed to stand in the full flame for ten to fifteen minutes. After cooling, the cover is removed, and if heating has not been too high, the residue is easily jarred from the crucible as one solid lump, which can then be broken up and transferred from a piece of paper into an Erlenmeyer flask of 500-cc. capacity.

Above the Erlenmeyer flask is placed a short reflux condenser, the upper end of which is closed by a two-holed rubber stopper. Through one hole of the stopper is inserted a 100-cc. dropping funnel. A bent glass tube for the escape of evolved hydrogen passes through the other. Water is slowly dropped upon the fusion residue until the excess hydride is broken up, much hydrogen being evolved the while. More water is added and a milk-like solution of calcium hydroxide and calcium sulfide is obtained. This is transferred to a liter beaker, diluted to 400–500 cc. and acidified with 100 cc. of concd. hydrochloric acid, allowing the heavier acid to run down the side of the beaker and not stirring. Stirring of the solution at this point means a loss of considerable hydrogen sulfide.

The beakers are allowed to stand for a few minutes and the solid matter therein dissolves in the acid. A clear solution will not always result but the turbidity will not interfere with the very pronounced starch–iodine end-point. The solution is now titrated with iodine, stirring gently at first, with starch solution as indicator. One cubic centimeter of the 0.1 N iodine is equivalent to 0.0016 g. of sulfur.

On the delicacy of this end-point it has been found the accuracy of the method depends. The end-point is not all that is to be desired as a little excess iodine is needed to yield a starch–iodine color to the whole solution. If the samples taken are too large, an overabundance of colloidal sulfur is formed which occludes some iodine and tends to lower results. It is well to add a slight excess of iodine and titrate back with standard sodium thiosulfate. With a little practice the end-point can be judged to less than one-half of a cubic centimeter, which is less than 0.0008 g. of sulfur. This would correspond to 0.15% sulfur in a 0.5-g. sample and is then the accuracy of the method. Results of analysis of potassium sulfate are given in Table II.

Samples 1–4, inclusive, are seen to give close approximations to the true sulfur content of the sulfate. These samples were treated as has been outlined.

Samples 5 and 6 were run as the others except that vigorous stirring

TABLE II

0.25 G. OF POTASSIUM SULFATE REDUCED TO CALCIUM SULFIDE WITH CALCIUM HYDRIDE

Sample K_2SO_4 = 18.37% sulfur

Sample	Iodine titer, cc.	Sulfur equiv., g.	Sulfur, %	Sample	Iodine titer, cc.	Sulfur equiv., g.	Sulfur, %
1	28.5	0.0456	18.24	5	22.0	0.0352	14.08
2	28.5	.0456	18.24	6	23.0	.0368	14.72
3	28.5	.0456	18.24	7	20.0	.0320	12.80
4	29.0	.0464	18.56	8	18.0	.0288	11.52

was carried on when acidifying the solution of the fusion residue. During this stirring the odor of hydrogen sulfide was noticed coming from the liquid and the iodine titer is quite low.

Samples 7 and 8 show the result of insufficient heating. It is not enough merely to heat until after a potassium flare is seen. The whole crucible must be heated to redness and kept in the full flame for several minutes. Fusion samples that were properly heated at redness for several minutes were tested for undecomposed sulfate and gave a negative test. The reduction is therefore quantitative. Any partial decomposition resulting in sulfite formation would not change results as the sulfite uses up iodine to the same extent as soluble sulfide. Little or no sulfite remains, however, as hydrogen sulfide may be evolved from fusion residues equivalent to all of the sulfur present. Results of analyses of barium, strontium and calcium sulfate are given in Tables III, IV and V.

TABLE III

0.25 G. OF BARIUM SULFATE REDUCED TO SULFIDE WITH CALCIUM HYDRIDE ($BaSO_4$, 13.6% OF SULFUR)

Sample	1	2	3 (0.5g.)	4
Iodine titer, cc.	21.5	21.5	42.5	21.5
Sulfur equiv., g.	0.0344	0.0344	0.0680	0.0344
Sulfur, %	13.76	13.76	13.6	13.76

TABLE IV

0.25 G. OF STRONTIUM SULFATE REDUCED TO SULFIDE WITH CALCIUM HYDRIDE ($SrSO_4$, 17.12% OF SULFUR)

Sample	1	2	3 (0.3 g.)
Iodine titer, cc.	26.5	26.5	32.0
Sulfur equiv., g.	0.0424	0.0424	0.0512
Sulfur, %	16.96	16.96	17.07

TABLE V

0.25 G. OF CALCIUM SULFATE REDUCED TO SULFIDE WITH CALCIUM HYDRIDE ($CaSO_4$, 23.55% OF SULFUR)

Sample	1	2	3 (0.3 g.)
Iodine titer, cc.	37.0	37.0	44.0
Sulfur equiv., g.	0.0592	0.0592	0.0704
Sulfur, %	23.68	23.68	23.46

Runs were attempted fusing 0.25 g. of lead sulfate with calcium hydride and treating as in the case of the other sulfates. The following reactions undoubtedly occur.

$$PbSO_4 + 4CaH_2 = PbS + 4CaO + 4H_2$$
$$CaH_2 \leftrightarrows Ca + 2H$$
$$Ca + PbS = CaS + Pb$$

This free lead is only slowly acted upon by the hydrochloric acid which is added prior to iodine titration. As a consequence iodine end-points are fading and results are high. An attempt was made to evolve hydrogen sulfide from the fusion residue as in determining sulfur in steel. The metallic lead as it dissolved, however, formed insoluble lead sulfide and thus held back some sulfur.

The method as outlined, then, is only applicable to non-volatile sulfur compounds free from metals which form acid-insoluble sulfides. Work is being carried on making calcium hydride fusions with volatile sulfur compounds in bombs.

Discussion of Results.—Probable chemical equations for the action of calcium hydride on any sulfate are as follows

$$MSO_4 + 2CaH_2 = MS + 2CaO + 2H_2O$$
$$MSO_4 + 4CaH_2 = MS + 4CaO + 4H_2$$

Since calcium hydride decomposes to some extent around 700°, it was thought that secondary reactions might occur

$$CaH_2 \leftrightarrows Ca + 2H$$
$$MS + Ca = CaS + M$$

Experiment verifies these last reactions even to the replacement of sodium and potassium by calcium. When potassium sulfate and calcium hydride ignitions were being made a potassium flare was noticed. When fusions of sodium thiosulfate and calcium hydride were made a sodium flare resulted. On examining the cover of the crucible after these latter fusions it was noticed that some sodium metal had condensed on the cooler cover, forming small globules.

It is evident from the tables that the method gives a quantitative estimation of sulfur in alkali and alkaline earth sulfates.

Insoluble alkaline sulfates are commonly determined for sulfur content by initial fusion with sodium carbonate to decompose the sulfate, followed by extraction of the sodium sulfate formed, ultimate precipitation of barium sulfate, and necessary filtering, drying, igniting, weighing and calculating. By the method herewith outlined sulfur may be estimated in insoluble sulfate samples within forty minutes.

Calcium hydride may be readily obtained and is easily powdered. It is a rather expensive chemical at present in that there is little demand for it in quantity. The cost of 7 g. of the hydride, or enough for one fusion, is about thirty-five cents. The saving of time and labor is the main merit of the method.

Summary

1. Calcium carbide has been studied as a reductant for sulfates. It is not as effective as calcium hydride.

2. Calcium hydride presents itself as a reagent for the quantitative reduction of alkaline earth and alkali sulfates to sulfides. From such fusion residues sulfur may be determined by iodine titration.

3. An example is given of replacement of potassium and sodium by calcium.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE FOOD RESEARCH LABORATORY AT THE MEDICAL COLLEGE OF THE STATE OF SOUTH CAROLINA, CHARLESTON]

THE POTATO AS AN INDEX OF IODINE DISTRIBUTION[1]

BY ROE E. REMINGTON, F. BARTOW CULP AND HARRY VON KOLNITZ

RECEIVED MAY 6, 1929 PUBLISHED OCTOBER 5, 1929

The theory that endemic thyroid enlargement is caused primarily by lack of iodine has been quite generally accepted by American scientists, so that studies on the occurrence of iodine in human environment are of considerable interest. McClendon and Williams[2] have shown that there is a correlation between shortage of iodine in surface water supplies and the incidence of goiter.

Numerous analyses by these and other workers have established that places in the United States where the water contains more than two parts per billion of iodine are few, and more than five parts per billion exceedingly rare. Von Fellenberg[3] concluded, as the result of an extended metabolism trial on himself, that the daily iodine requirement for a man is 14 micrograms, which is a great deal less than the amount (300 to 400 milligrams per year) recommended by Kimball[4] for goiter prophylaxis in the United States. Even if inorganic compounds of iodine are efficiently utilized in the body, water alone cannot supply the requirement in more than a very restricted area. Hence McClendon[5] turned his attention to vegetable foods, and was able to show that foods from Maine and Connecticut contain more iodine than do those from Minnesota or Oregon.

The senior author of this paper[6] has called attention to the relatively large amounts of iodine present in root and leafy vegetables from South Carolina, analytical data for which are now presented in Table I, and

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[1] Presented before the Division of Agricultural and Food Chemistry at the 77th meeting of the American Chemical Society, Columbus, Ohio, April 29–May 3, 1929.

[2] J. F. McClendon and Agnes Williams, *J. Am. Med. Assocn.*, 80, 600 (1923).

[3] Th. von Fellenberg, *Biochem. Z.*, 142, 246 (1923).

[4] O. P. Kimball, *J. Am. Med. Assocn.*, 91, 454 (1928).

[5] J. F. McClendon and J. C. Hathaway, *ibid.*, 82, 1668 (1924).

[6] Roe E. Remington, *Science*, 68, 590 (1928).

TABLE I

IODINE CONTENT OF VEGETABLE FOODS FROM GOITROUS AND NON-GOITROUS REGIONS

Parts per billion, *dry* basis

	South Carolina Analyses by Remington	California Analyses by McClendon	Oregon Analyses by McClendon
Lettuce	761	..	..
Summer squash	716	..	..
Spinach	694	26.0	19.5
Turnip tops	433	..	..
String beans	429	..	29
Cabbage	336	..	..
Asparagus	285	12.0	..
Beets	227	8.0	..
Turnips	223		
Potatoes	211	..	..
Carrots	197	8.5	2.3
Sweet potatoes	98	..	..

McClendon[7] has published analyses of vegetables from California. Mitchell[8] has also examined a number of samples of South Carolina vegetables and feeds, and finds a tendency to higher iodine content in that part of the state which is more distant from the coast and nearer the Blue Ridge of the Appalachian Mountains. He reported marked differences in the results on samples of the same product from the same general locality, which differences have been found by us to amount to two or three hundred per cent. At first we were inclined to attribute the lack of uniformity to errors in laboratory technique, but extended experimentation has convinced us that the differences actually exist in the crops as grown. So far we have no suggested explanation, although soil type, stage of maturity of the crop at harvest, fertilizer and soil treatment, and rainfall all deserve consideration.

The salt spray theory of iodine distribution seems to have gained general acceptance, but the Atlantic Ocean contains only 23 parts per billion of iodine, and five or six parts per billion in the water of streams cannot come solely from spray unless the waters contain a like proportion of the other salts of the sea, which they do not. Mitchell[8] found six parts in the water of the Broad River at a point 150 miles from the coast, but the Broad River is not brackish. Lunde[9] believes that in the cooling of the earth iodine was distributed throughout all phases, and hence is now found in rocks, soils, and in the air and sea, but has been leached out of the soils of some areas. Von Fellenberg[10] found several hundred parts per billion in igneous rocks.

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[7] J. P. McClendon and Roe E. Remington, THIS JOURNAL, 51, 394 (1929).

[8] J. H. Mitchell, Clemson College Bulletin 252, 1928.

[9] G. Lunde, *Tids. Kemi Bergvesen*, 7, 61, 67 (1927).

[10] Th. von Fellenberg, *Biochem. Z.*, 152, 132 (1924).

Examination of a large number of samples has heretofore been difficult owing to the intricate and laborious technique of the oxygen combustion method of McClendon, which has been the most reliable method in use up to the present time. It has been found in this Laboratory, however,? that if the organic matter were destroyed by simple ignition in a porcelain dish at a temperature which did not exceed 450°, 95% of the iodine in sodium iodide added to potatoes could be recovered, and we have since obtained as good or better recovery when 0.1 g. of dried thyroid is added to 100 g. of dried potatoes; hence we conclude that organic as well as inorganic iodine is retained by the ash of vegetables when ignited at this temperature. The method is so simple that a good technician can now make six to eight determinations per day if laboratory facilities are adequate.

In order to compare the iodine content of foods in maritime and non-maritime regions, it seemed desirable to choose a crop which is universally grown, largely used as food, and can be readily obtained and transported without spoilage. Cereal grains are not suitable because their iodine content is very low, regardless of where grown. Since we have found that Irish potatoes from South Carolina contain as much iodine as any other root crops which we have examined, the potato was chosen as the basis of our survey. Samples in South Carolina were collected by county agricultural agents; those from other states were furnished us through the courtesy of the directors of the several agricultural experiment stations.

On receipt the samples were washed, cut into small cubes without peeling, dried first for twenty-four hours or more by a current of air at room temperature blown upward through the screen wire bottoms of trays in which the samples were placed, and finally for twenty-four hours in an oven at 80°, after which they were ground and bottled. The moisture content of the dried samples ranged from 1 to 3%. The loss in drying varied in different samples between 75 and 80%. Results are given in Table II.

The Idaho samples were all produced on wind-borne silt loam soils of volcanic origin, fertilized with liberal quantities of stable compost but no commercial fertilizer. Mixed commercial fertilizers are extensively used in Michigan, Maine and South Carolina, but not in Minnesota nor North Dakota.

With regard to South Carolina, while 72 is probably not a sufficient number of samples on which to base an accurate study, it has seemed worth while to analyze the data, first with reference to distance from the sea and second with regard to soil types. If we draw lines across the map of the state at intervals of fifty miles from the coast, and average the samples within each belt, we obtain the values in Table III. There is a regular progressive increase in iodine content as we go from the coast toward the mountains.

TABLE II

IODINE CONTENT OP POTATOES PROM DIFFERENT REGIONS

Sample no.	Source	Locality	Iodine in parts per billion, dry basis
212	Idaho	Twin Falls	160
294	Idaho	Moscow	125
306	Idaho	Hansen	45
		Average	110
129	Maine	Monmouth	203
133	Maine	Brunswick	283
137	Maine	Orono	188
138	Maine	Presque Isle	105
		Average	195
195	Michigan	Pontiac	120
161	Michigan	Greenville	110
168	Michigan	Manton	69
297	Michigan	Chatham	75
		Average	97
139	Minnesota	Grand Rapids	67
140	Minnesota	Grand Rapids	117
141	Minnesota	Grand Rapids	75
143	Minnesota	Grand Rapids	26
144	Minnesota	Grand Rapids	70
145	Minnesota	Grand Rapids	109
146	Minnesota	Grand Rapids	125
147	Minnesota	Grand Rapids	98
		Average	86
148	North Dakota	Fargo	78
	South Carolina	72 samples	87 to 544
		Average	211

TABLE III

IODINE CONTENT OP POTATOES IN RELATION TO DISTANCE FROM THE SEA

Parts per billion, dry basis

Distance from sea, miles	0-50	50–100	100–150	150–200	200
Number of samples	19	18	15	16	4
Iodine content, average	180	213	223	249	266

With regard to soil types, the state is roughly bisected by the "fall line," which marks a prehistoric coast (Fig. 1). Below the fall line the soils are predominantly sand or sandy loam, and have come up out of the sea in comparatively recent geologic time. Above the fall line the predominating type is a red clay loam, brought down by erosion from the granite rocks of the Appalachian system. The differentiation is not sharp, and some areas of clay have been washed clear down into the lower pine belt. It is rational to expect that the remains of marine plants and animals which are incorporated in the soils below the fall line will have an effect on the iodine content of crops raised thereon. It will be noted, however, that the samples from the Piedmont (Table IV) (above the fall line) are richer in iodine than those from any of the lower areas, not excepting the coast itself. In fact, were it not for the sand hill section and the narrow coastal belt, the order would be the same as that of the previous table. The soil of the sand hills is particularly barren, and presents an agricultural problem of its own, while we can believe that the higher values along the coast (as compared with the lower pine) are due to the immediate effect of the

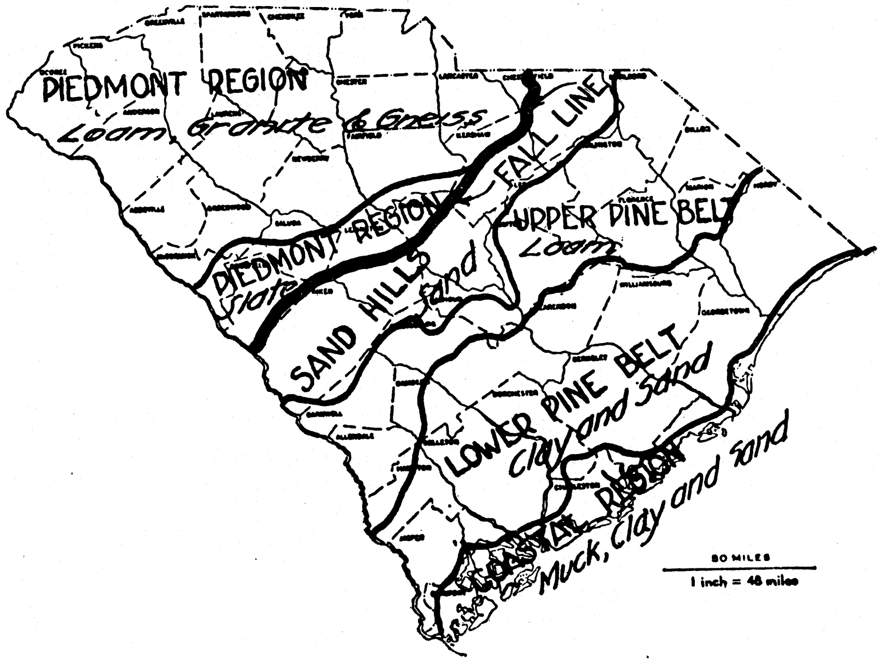

Fig. 1.—General topographic and soil areas of South Carolina.

TABLE IV

IODINE CONTENT OF POTATOES IN RELATION TO SOIL AREAS

Parts per billion, dry basis

Soil area	Number of samples	Iodine content, av.
Coastal Region	7	198
Lower Pine Belt	18	164
Upper Pine Belt	12	234
Sand Hills	7	191
Piedmont	28	249

sea, in that marsh grass is used as feed for live stock and for fertilizer, seaweed is blown ashore and finds its way into the soil, and the possible effect of sea spray. It is a matter of common agricultural knowledge that the clay soils of the Piedmont not only hold water better, but also retain mineral salts, so that only one-fourth to one-half as much fertilizer is used to make a crop as is required in the sandy soils of the low country.

Commercial fertilizers have probably been used for a longer time, and more abundantly in South Carolina than in any of the interior states. Chilean nitrate may carry as high as 0.02% of iodine[11] but the amounts reported for other usual fertilizer materials are not higher than have been found in many soils. As previously noted, fertilizers were used in producing all the samples from Michigan, where lower amounts of iodine were found. We believe that the main source of iodine in South Carolina vegetation lies in the disintegration of the granitic rocks of the Blue Ridge, and that this has been supplemented by the liberal use of commercial fertilizers over a period of years. This supply of iodine is being conserved by the return of vegetable matter and animal wastes to the soil.

Summary

Analyses of 72 samples of Irish potatoes from different parts of South Carolina, as well as of samples from Maine, Michigan, Minnesota, North Dakota and Idaho, are presented and discussed in relation to various factors which have been supposed to influence the iodine content of plants. Average values are: South Carolina 211, Maine 195, Idaho 110, Michigan 94, Minnesota SG.

Large variations are found in samples from the same area and identical soil type, the variations, however, not being confined to South Carolina. Average values increase progressively from the sea to the Appalachian Mountains, but the relative amount of clay in the soil increases in the same manner. It is suggested that the principal source of the iodine is from the disintegration of granite rocks, supplemented by the use of commercial fertilizers. The immediate influence of the sea is not seen beyond a very narrow belt along the coast.

CHARLESTON, SOUTH CAROLINA

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[11] Th. von Fellenberg, *Mitt. Lebenson. Hyg.*, **15**, 247 (1924).

[CONTRIBUTION NO. 17 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

INTENSIVELY DRIED CARBON TETRACHLORIDE

BY SAM LENHER

RECEIVED JUNE 1, 1929 PUBLISHED OCTOBER 5, 1929

Recently, in an extension of his work on intensively dried liquids, H. B. Baker[1] has reported vapor density measurements on eight liquids dried for from two to fifteen years which indicate an increase in molecular weight on drying.

Last year boiling-point determinations were carried out on benzene and carbon tetrachloride which showed no change in boiling point on prolonged drying.[2] The present paper describes some further measurements on intensively dried carbon tetrachloride.

Carbon tetrachloride was prepared in exactly the way described previously.[2] It was sealed up, as before, in specially prepared, capillary-free, hard glass tubes together with redistilled phosphorus pentoxide. The tube, which had an external diameter of 18 mm. with 2-mm. walls, was heated to softening before the introduction of the phosphorus pentoxide. The redistilled pentoxide was introduced into the dry tube by plunging a dry glass tube into the pentoxide and forcing it into the drying tube with a glass rod. This operation prevented the pentoxide from coming into contact with atmospheric moisture except possibly at the ends of the tube. The tube was sealed up on June 19, 1924. Care was taken to thicken the glass where the tube was sealed off. The tube was allowed to stand at room temperature.

This tube was opened on May 15, 1929; the drying time was five years. The boiling point of the dry carbon tetrachloride was measured in a platinum wire boiling-point apparatus[3] under conditions where there was less than 0.03' of superheating. The boiling point of the carbon tetrachloride, measured three minutes after the drying tube was opened, was 76.8° at 762.2 mm. No difference in temperature could be observed between the boiling liquid and the vapor 1–2 cm. above the liquid. The thermometer used had been compared with Bureau of Standards thermometer No. 35388.

The boiling point was then determined using the procedure adopted by Baker for his boiling-point measurements. The carbon tetrachloride from this boiling-point determination was placed with the same thermometer in a straight tube of 2-cm. diameter and heated in a Nujol-bath. The carbon tetrachloride did not begin to boil until the thermometer in the liquid registered 90°. Boiling was then not violent, but was quiet and regular and gave no indication of superheating other than the reading on the thermome-

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[1] Baker, J. *Chem. Soc.*, 1051 (1928).

[2] Lenher and Daniels, *Proc. Nat. Acad. Sci.*, 14, 606 (1928).

[3] Mathews, *Trans. Am Electrochem. Soc*, 19, 81 (1911).

ter. The carbon tetrachloride was not entirely free of dust particles and of tiny bits of phosphorus pentoxide. This experiment shows clearly the difficulty of avoiding superheating when a boiling point is measured in this way.

The molecular weight of the intensively dried carbon tetrachloride was measured by the method of Victor Meyer. The familiar form of the Victor Meyer apparatus was used,[4] the only innovation being that mercury was used in the gas buret. The intensively dried carbon tetrachloride was introduced directly into small bulblets from the dry tube by dipping the open capillary end of the warmed bulblets into the liquid and allowing them to cool. The bulblets were weighed and the vapor density of the carbon tetrachloride was measured in the apparatus which had been previously evacuated for four hours at the boiling point of aniline. The measurements were carried out at the boiling point of aniline. The six measurements were made over a period of an hour and a half after the opening of the drying tube. The molecular weight of intensively dried carbon tetrachloride in six experiments was found to be 160.1, 149.9, 153.8, 152.1, 154.5, 154.9; the molecular weight of ordinary carbon tetrachloride is 153.8.

The phosphorus pentoxide in the drying tube was treated with water in a calorimeter to determine how much unused pentoxide remained after five years' contact with carbon tetrachloride. When the tube was opened the pentoxide was in a finely divided state, giving no sign of formation of phosphoric acid. This test showed that **3.5** g. of phosphorus pentoxide was still present when the tube was opened. This figure is at least 30% too low, because of the difficulty of transferring the pentoxide to the calorimeter without heat loss.

The criticism cannot be made that the drying time was insufficient to effect intensive drying for the writer's carbon tetrachloride which showed a normal boiling point and normal molecular weight by the vapor density method was dried for five years, while Baker[1] reports a molecular weight of 191 for carbon tetrachloride dried for three years and a molecular weight of 201 for the same substance dried for five years.

The writer[5] has been able to observe some of the phenomena described by Baker[1] for dried liquids and liquids subjected to electrical potential with ordinary liquids under as nearly as possible the same experimental conditions. These experiments which will be described elsewhere[6] will show that superheating is an important factor in Baker's experiments.

It may be remarked that Briscoe, Peel and Robinson[7] have recently measured with great care the density and surface tension of benzene dried

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[4] Findlay, "Practical Physical Chemistry," Longmans, Green and Company, London, 1923, 4th **ed.**, p. 43.

[5] Lenher, *Nature*, 123,907 (1929).

[6] Lenher, J. Phys. *Chem.*, October (1929).

[7] Briscoe, Peel and Robinson, **J.** *Chem. Soc.*, 368 (1929).

for eighteen months and have found no change which would justify an assumption of a change in degree of association on drying.

Summary

Carbon tetrachloride which has been in contact with pure phosphorus pentoxide in a sealed tube for five years at room temperature shows no change in boiling point or molecular weight, by the Victor Meyer vapor density method, which can be attributed to intensive drying and consequent change in degree of association.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE VISCOSITY OF AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES WITH SPECIAL REFERENCE TO BARIUM CHLORIDE

BY GRINNELL JONES AND MALCOLM DOLE

RECEIVED JUNE 12, 1929 PUBLISHED OCTOBER 5, 1929

Introduction

A number of related properties of barium chloride solutions have been determined with a high precision over a considerable range of concentration in the hope that a study of the data in the light of modern theories of solutions might reveal new relationships between the properties and new laws for the variation of the properties with the concentration. The first paper[1] of this series records the results of measurements of transference numbers by both the analytical- and electromotive-force methods which resulted in the discovery of a new and exact relationship between the transference number and the concentration. This, the second paper of the series, records measurements at 25° of the viscosity of barium chloride solutions relative to that of water, over the range 0.005 to 1.0 molal. This investigation has resulted in the discovery of a new exact relationship between the fluidity and the concentration. A later paper will give data on the conductivity of the same solutions.

Historical **Review.**—Poiseuille,[2] the great pioneer in research on viscosity, found that some salts increase the viscosity of water whereas others decrease the viscosity. Sprung[3] appears to have been the first to measure solutions of barium chloride and found that it increased the vis-

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[1] Grinnell Jones and Malcolm Dole, THIS JOURNAL, 51, 1073 (1929). We regret that in this paper we implied that Washburn found it necessary to filter his solutions during his work on transference numbers [THIS JOURNAL, 31, 322 (1909)]. This implication is, however, misleading as Washburn actually avoided the filtration of his solutions.

[2] Poiseuille, Ann. *chim. phys.*, [3] *21*, 76 (1847).

[3] Sprung, Ann. *Physik*, 159, *1* (1876).

cosity of water. Arrhenius[4] made some viscosity measurements on solutions. He found that the change in viscosity caused by the addition of a salt was roughly proportional to the concentration at low concentrations but increased more rapidly than the concentration at moderate concentrations (1 normal). He proposed a new formula for the relationship between viscosity and concentration, namely, $\eta = A^c$, where η is the relative viscosity compared to that of water at the same temperature and A is a constant for any given salt and temperature. This equation has been tested by Reyher,[5] by Wagner[6] and by others and found to hold within a few tenths of 1 per cent. between $^1/_8$ and $^1/_2$ normal and within about 1% up to 1 normal.

Sutherland[7] suggests that the depolymerization of triple water molecules by the dissolved salt causes diminution in viscosity.

The next outstanding investigator on this subject was Grüneisen,[8] who made a careful and critical study of the experimental technique with the Ostwald form of viscometer and then made measurements, which are probably more precise than any previously made, on aqueous solutions of sixteen salts and of sucrose over a wide range of concentration. Grüneisen made measurements with more dilute solutions than his predecessors and thereby discovered that the viscosity–concentration curves, instead of becoming more nearly straight at the dilute end, exhibit a negative curvature. This behavior is not in accord with Arrhenius' equation which must, therefore, be regarded as invalid, even as a limiting law for low concentrations. Grüneisen found that both the salts which increase the viscosity and those which decrease the viscosity show a negative curvature of the viscosity–concentration curves at low concentrations. The viscosity-concentration curves for salts which increase the viscosity are so nearly straight lines that the deviations would not be readily apparent on the scale which could be printed on this page, but the deviations are clearly systematic and greater than the experimental error. For a salt which increases the viscosity of water, the curve starts at $\eta = 1.0000$ when $c = 0$ with a positive but diminishing slope, giving a negative curvature, then straightens out, passes through a point of inflection at moderate concentrations (about 0.3 molal), and then the curvature becomes slightly positive. These changes in the curve are more apparent if, following a suggestion of Grüneisen, we plot $(\eta - 1)/c$ against c (or some root of c for the sake of spreading out the points at the lower concentrations). $(\eta - 1)/c$ is strictly the slope of the chord connecting a point on the $\eta - c$ curve with the origin, but it is approximately the same as the slope of the $\eta - c$ curve at the same point.

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[4] S. Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

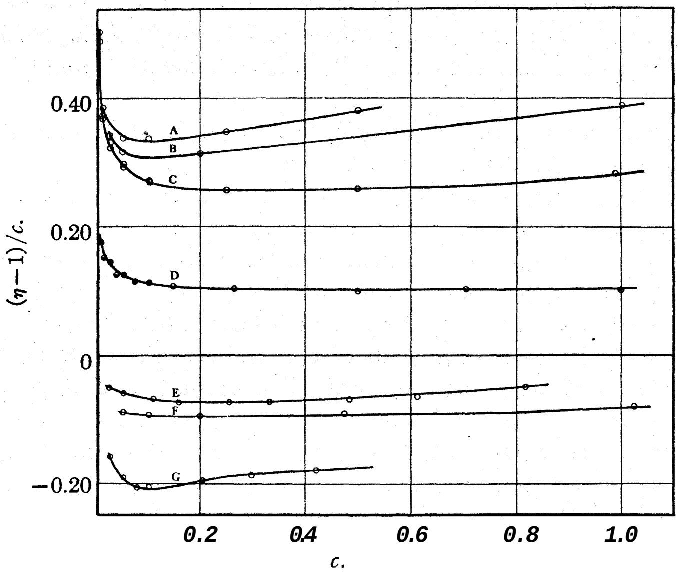
[5] R. Reyher, *ibid.*, 2, 744 (1888).

[6] J. Wagner, *ibid.*, 5, 31 (1890).

[7] W. Sutherland, *Phil.* Mag., [5] **50**, 481 (1900).

[8] E. Grüneisen, *Wiss. Abh. Phys. Techn. Reichsanstalt*, **4**, 151, 237 (1905).

If the relationship between the viscosity and concentration were a linear one, $(\eta - 1)/c$ would be a constant and its plot would be a straight line parallel with the c axis. Figure 1 gives such curves for several salts (magnesium sulfate (A), lithium iodate (B), potassium iodide (F) from data by Grüneisen; lithium nitrate (D) from data by Grüneisen and by Applebey; cesium nitrate at 25° (E) and at 0° (G) from data by Merton; and the data on barium chloride (C) reported below in this paper). As will be seen, the values of $(\eta - 1)/c$ decrease rapidly with increase of concentration at low concentrations, pass through a minimum and then slowly rise. A downward slope in this curve corresponds to a negative curvature in the $\eta - c$ curve. Grüneisen's paper gives similar curves for many other salts. Grüneisen proposed the equation



Curve A, $MgSO_4$ at 18° after Grüneisen; *B*, $LiIO_3$ at 18° after Grüneisen; C, $BaCl_2$ at 25°, Jones and Dole; D, $LiNO_3$ at 18° ◒ Applebey, ● Grüneisen; E, $CsNO_3$ at 25° after Merton; F, KI at 18° after Grüneisen; G, $CsNO_3$ at 0° after Merton.

Fig. 1.—$(\eta-1)/c$ against c.

$$\eta = 1 + Aic + B(1 - i)c + Cc^2$$

where i is the degree of dissociation as computed from the conductivity and A, B and C are constants for any given salt and temperature. *A* is supposed to represent the effect of the friction of the ions on the water, B that of the un-ionized molecules on the water and C that of the ions and molecules on each other. Grüneisen was able to select values for the empirical constants to make the equation fit his data, although negative values of A and B had to be selected in many cases, However, his equation is not a useful interpolation formula permitting the computation of the viscosity at any concentration owing to the presence of the parameter i, which is itself a function of the concentration. Grüneisen pointed out that the smaller the electrical mobility of an ion the greater is its influence in increasing the viscosity of solutions.

Schneider[9] has made measurements similar to Grüneisen's with many other salts, although with less precision, and obtained similar results, showing that Grüneisen's observation of negative curvature of the viscosity–concentration curves at low concentrations is a general one. He made no advance in the interpretation of the phenomena.

Among the many investigators of the viscosity of solutions the next who deserves mention in this brief review is Applebey,[10] who made careful measurements at 25, 18 and 0° on solutions of lithium nitrate, a salt which increases the viscosity of water. Applebey's work extended over a wide range of concentration, including solutions even more dilute ($c = 0.00724$) than those studied by Grüneisen. His results show that the negative curvature becomes more pronounced at very low concentrations (see Fig. 1, Curve D) and that the curvature in this region is much greater than would be predicted by Grüneisen's equation. He also showed that the negative curvature becomes greater as the temperature is lowered. Applebey made the suggestion that when a salt is dissolved in water there are two different effects on the viscosity: (1) a depolymerization of triple water molecules, $(H_2O)_3$, to form single molecules, which tends to diminish the viscosity; (2) an increase in viscosity due to the presence of the ions of the salt and the un-ionized molecules of the salt. It is assumed that the friction depends primarily on the size of the ion or molecule. In the case of salts composed of ions which are not greatly hydrated, such as the Cs^+, Rb^+, K^+, NH_4^+, I^-, Br^- or NO_3^- ions, the increase due to the friction of the ions on the water is less than the diminution of the viscosity due to depolymerization of the water, giving a net decrease in viscosity or a negative slope of the viscosity-concentration curve. Most ions, however, are sufficiently hydrated so that the increase in viscosity due to their presence more than offsets the decrease due to depolymerization, giving a net increase in viscosity with concentration. Applebey attempted to derive an equation connecting viscosity and concentration but the equation which he obtained contains the degree of dissociation of the salt computed from the conductivity, the association factor of water, and the hydration numbers of the ions (the number of molecules of water attached to each ion to form the hydrated ion). However, the exact form of the function connecting any of these variables with the concentration is unknown, and, therefore,

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[9] K. Schneider, "Dissertation," Rostock, 1910.

[10] M. P. Applebey, *J. Chem. Soc.*, 93, 2000 (1910).

Applebey's equation does not give even by implication the exact functional relationship connecting viscosity and concentration. In order to make his equation give any negative curvature at low concentrations, it was necessary for him to assume that the ions have a greater friction against the water than the un-ionized salt, which is hardly in accord with his assumptions that the volume of the particles is the important factor in the viscosity, or else that the ions are less effective than undissociated salt molecules in depolymerizing the water. But even with these assumptions, his equation cannot predict the rapid change in slope which actually occurs and, of course, the modern view that solutions of strong electrolytes are completely dissociated makes the attempt to account for the negative curvature in this manner entirely illusory. Applebey used his equation as a means of computing hydration numbers of the ions and obtained results for lithium nitrate which he regarded as plausible, but for cesium nitrate he obtained negative hydration numbers which are obviously absurd. Curve D in Fig. 1 shows the good agreement between Grüneisen's and Applebey's data on lithium nitrate at 18° and also the sharp curvature at low concentrations.

The viscosity-concentration curves for salts which diminish the viscosity of water are more complicated than for salts which increase the viscosity. The behavior at extreme dilutions has never been adequately investigated, but at the lowest concentrations for which data are available the curve has a slight negative curvature. These curves then pass through a point of inflection at moderate concentrations (about 0.1 to 0.2 molal), and have a positive curvature at all higher concentrations. The viscosity passes through a minimum in the neighborhood of one molal and has a positive slope at higher concentrations and at very high concentrations may again become greater than that of water.

The work of Merton[11] on cesium nitrate appears to be the most accurate and extensive study of a salt which diminishes the viscosity of water. His work confirms the observation of Applebey on lithium nitrate that at low temperatures negative slopes and negative curvatures are more pronounced than at higher temperatures. Merton made no theoretical advances. His data on cesium nitrate are shown in Fig. 1, Curves E and G.

The various hypotheses which have been suggested to account for "negative viscosity" are discussed at considerable length by Rabinovich.[12] He concludes that depolymerization of water molecules must be responsible for "negative viscosity."

It is apparent that although the general shape of the viscosity-concentration curves has been established, the phenomena at extreme dilutions have not been adequately investigated, and no one has yet found an exact general equation connecting viscosity and concentration.

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[11] T. R. Merton, *J. Chem. Soc.*, **97**, 2454 (1910).

[12] A. I. Rabinovich, THIS JOURNAL, **44**, 954 (1922).

Measurements of the viscosity of barium chloride solutions have been carried out by Sprung[3] at 18°, by Arrhenius[4] at 17.6°, by Wagner[6] at 25°, by Schneider[9] at 18° and by Herz[13] at 25°. Although the earlier work makes it clear that barium chloride increases the viscosity of water, the available data on this salt are lacking in precision and do not cover the lower range of concentration.

Experimental Part

The viscometer was of the Ostwald type made of quartz in accordance with the recommendations of Washburn and Williams,[14] except that a small bulb was blown between the lower mark on the upper reservoir and the capillary as suggested by Chadwell.[15] The capillary was 17.0 cm. long and its effective average radius was 0.026 cm. All measurements were made at 25°. The thermostat showed an extreme variation during the experiments of only 0.003°. The viscometer was permanently mounted in a stiff brass frame which was designed so that it could be attached to a rigid frame in a definite position inside the thermostat; but in spite of our efforts to ensure stability and reproducibility in the mounting, a major operation on the building produced an unavoidable disturbance in the mounting of the viscometer. During the first part of the work one end of the building (the Jefferson Physical Laboratory) was supported on jacks while repairs were being made on the foundations. During this period the time of flow of water in our viscometer was 342.54 seconds (see Table I). Then during the period beginning on August 30 and completed on September 2, the jacks were lowered, permitting one end of the building to move onto its new foundations. Following this event we found that the water value of our viscometer had changed to 342.33 seconds, or 0.21 second faster (see Table I). The data are therefore divided into two series, the first series including all measurements before September 2, which are computed with 342.54 as the water value, and the second series all made after this date which are computed with 342.33 seconds as the water value. The concentrations are expressed in gram molecules of barium chloride per liter. All of the data for a given concentration are grouped together in the table to facilitate comparison and averaging. In comparing the time of flow of an experiment in the first series with one in the second, proper allowance must be made for the change in the water value.

We found it advisable to fill the viscometer with sulfuric-chromic acid cleaning mixture and allow it to stand overnight at frequent intervals to ensure proper drainage. In order to avoid dust particles, everything that went into the viscometer—the water, the solutions, the cleaning mixtures and wash waters and the air used to dry the instrument between experiments—was passed through a sintered Jena glass filter. After this precaution was adopted only one experiment out of 39 had to be rejected on account of dust particles, which shows that this filtration was very helpful.

The so-called kinetic energy correction has been applied in accordance with the method recommended by Bingham,[16] but since there is some question as to the magnitude of this correction[17] we give our results both with and without the correction and have designed our viscometer so as to make the correction small. In our experiments this

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[13] W. Herz, Z. *anorg.* Chem., 89, 393 (1914).

[14] E. W. Washburn and G. T. Williams, THIS JOURNAL, 35, 737 (1913).

[15] H. M. Chadwell, *ibid.*, 48, 1915 (1926).

[16] See E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, 1922, p. 18.

[17] N. E. Dorsey, Phys. *Rev.*, 28, 833 (1926); W. Riemann III, THIS JOURNAL, 50, 46 (1928).

correction has its maximum value of 0.14% with the molar solutions and falls off with dilution to 0.013% with 0.1 molar solution.

Measurement of Time of Flow.—The standard clock of the Jefferson Physical Laboratory, which has been proved by many tests to be sufficiently constant for our purpose, was used as our time standard. This clock has an attachment which gives a momentary electric impulse once every second. By means of a relay and induction coil the electric impulses from the clock produced a spark between two platinum points every second. This spark burned a hole in moving paper tape (stock market ticker tape) which passed at a constant velocity through the spark gap. The moment of passage of the meniscus past the marks was recorded on the same tape by touching a tapping key which also produced a spark. The motor which drove the paper tape was designed as a constant speed motor and a constant speed governor of the centrifugal type was added. The velocity of the tape was adjustable by means of the governor and in the final experiments was always within the limits of 9 to 12 cm. per second. Careful test indicated that this device recorded the moment of touching the tapping key within 0.01 second. There is, however, a psychological lag of unknown and variable amount between the observation of the passage of the meniscus past the mark and the tapping of the key with the finger. If this lag were equal at the beginning and the end of the time interval being measured, it would make no error. Therefore, the shape of the

TABLE I

RECORD OF EXPERIMENTAL DATA ON TIME OF FLOW OF WATER THROUGH VISCOMETER AT 25°

Series I

Time

	342.54	342.67	342.60	342.59	342.58	342.51
	342.44	342.70	342.56	342.61	342.57	342.52
	342.46	342.59	342.55	342.52	342.67	
	342.48	342.65	342.52	342.47	342.59	
	342.47	342.60	342.57	342.49	342.51	
	342.48	342.49	342.58	342.49	342.64	. . .
	342.53	342.60	342.55	342.51	342.55	
	342.50	342.62	342.59	342.57	342.53	
	342.46	342.67	342.55	342.52	. . . .	. . . .
	342.51	342.57	. . .	342.49		. . .
	342.49	342.59	. .	342.49	. .	. .
	342.51	342.62		342.49		
	. . .	342.63	. .	. .	. .	
	. . . .	342.63	. . . .	. . . .	. .	. . .
Average	342.49	342.61	342.56	342.52	342.58	342.51

Mean for Series I, 342.54 seconds.

Series II

Time

	342.35	342.28	342.32	342.28	342.35	342.35	342.34	342.36	342.34
	342.35	342.25	342.26	342.28	342.30	342.34	342.38	342.40	342.34
	342.31	342.39	342.26	.	342.32	. . . .	.	342.38	. . . .
	342.31	342.30	. . .	. . . .				. .	
	342.34	342.27	. . . .	. . . .	. . . .	. . . .		. . .	. . .
Average	342.33	342.30	342.28	342.28	342.32	342.35	342.36	342.38	342.34

Mean for Series II, 342.33 seconds.

viscometer at and immediately above the upper and lower marks was made as nearly identical as possible by an expert glass blower and care was taken to ensure that both marks were equally well illuminated in order that the two events being timed should be as nearly as possible identical. Much practice is also helpful in attaining precision, just as it is in many other endeavors which depend upon exact coördination of eye and hand. During the first series, the time of flow with water was measured 57 times on six different days with six independent fillings of the viscometer, giving an average of 342.54 seconds. The extreme variation between the highest and lowest of the 57 measurements was 0.26 second. The average was probably correct within 0.03 second or 0.01%. (The probable error of the mean when computed by Bessell's formula is 0.005 second.) During the second series with nine different fillings with water and 27 measurements, the average was 342.33 seconds and the extreme variation was 0.15 second. For the reasons explained above these averages are not comparable.

The experimental data on water are recorded in Table I and the solutions in Table II. The viscometer was cleaned, dried and refilled with water or barium chloride for each experiment. From 2 to 14 runs were made on

TABLE II

VISCOSITY OF BARIUM CHLORIDE SOLUTIONS AT 25°

Gram mole/ liter	Density, d_c	Av. time, sec., t_c	Water value, sec., t_0	$\frac{d_c t_c}{d_0 t_0}$	Kinetic corr.	Viscosity, η	Correction to round concn.	Viscosity, η at round concn.
0.004996	0.99823	342.76	342.33	1.00242	$+0.0000_2$	1 00244	+0	1.00244
.005000	.99819	342.80	342 33	1.00250	$.0000_2$	1.00252	+0	1.00252
						Mean η at c = 0.005,		1.00248
.010055	99887	342 97	342.33	1.00368	$.0000_3$	1.00371	−0.00001	1.00370
,009990	99881	343 00	342.33	1.00369	$.0000_3$	1.00372	+0	1.00372
						Mean η at c = 0.01,		1.0037_1
.024988	1 00161	343.51	342.33	1.00802	$.0000_5$	1.00807	+0	1.00807
.024995	1.00160	343.61	342.33	1.00830	$.0000_5$	1.00835	+0	1.00835
						Mean η at c = 0.025,		1.0082_1
.048598	1 00587	344.34	342.54	1 01413	$.0000_8$	1.01421	$+0.0003_5$	1.0145_6
.048598	1.00587	344.39	342.54	1.01427	$.0000_8$	1.01435	$+\ .0003_5$	1.01470
,049960	1.00615	344.24	342.33	1.01474	$.0000_8$	1.01482	$+\ .0000_1$	1.01483
,049960	1 00615	344.25	342.33	1.01477	$.0000_8$	1.01485	$+\ .0000_1$	1.01486
						Mean η at c = 0.05,		1.01474
.09996	1.01520	345.30	342 33	1 02702	$.0001_3$	1.02715	$+\ .0000_1$	1.0271_6
.09996	1.01520	345.28	342.33	1.0269_6	$.0001_3$	1.02709	$+\ .0000_1$	1.02710
.09997	1 01497	345.25	342.33	1.02664	$.0001_3$	1.02677	$+\ .0000_1$	1.02678
.09997	1 01497	345 35	342.33	$1\ 0269_3$	$.0001_3$	1.02706	$+\ .0000_1$	1.02707
.09997	1 01497	345.33	342 33	1 02687	$.0001_3$	1.02700	$+\ .0000_1$	1.02701
						Mean η at c = 0.10,		1.02704
.24990	1 04212	348.55	342.33	1.06417	$.0002_8$	1.06445	$+\ .0000_3$	1.06448
.24990	1 04212	348.47	342.33	1.06393	$.0002_8$	1.06421	$+\ .0000_3$	1.06424
.24948	1 04210	348.50	342.33	1.06400	$.0002_8$	1.06428	$+\ .0001_3$	1.06441
						Mean η at c = 0 25,		1.06438
.4972	1.08663	354 61	342.54	1.12822	$.0005_6$	1.12878		
.4972	1.08663	354.65	342 54	1.12835	$.0005_6$	1.12891		
.4959	1.08640	354 46	342.33	1.1282_0	$.0005_6$	1.1287_6[a]		
				Mean η at c = 0.4972,		1 12893		
.9913	1.17358	372 26	342.54	1.27915	$.0014_4$	1.28059		
.9913	1.17358	372 20	342.54	1.27895	$.0014_4$	1.2803_9		
				Mean η at c = 0.9913,		1.28049		

[a] This figure is corrected to c = 0.4972 by adding $+0.0003_5$, giving 1.12911 and averaged with the two above, giving 1.12893.

each filling and the time of each is recorded in Table I to show the concordance of the data. The average time only is recorded for the solutions to save space.

Analysis and Interpretation of our Data on Barium Chloride.—The data recorded in Table II were then brought to round concentrations by applying very slight corrections and then averaged, except in the case of the two higher concentrations where the concentrations actually used were so far from the round concentrations that any attempt to correct them was thought to be inadvisable at this stage of the interpretation of the data. The viscosities thus obtained are shown in Col. 2 of Table III. Then we plotted the viscosity against the concentration and obtained a curve which is approximately straight but with a negative curvature at the dilute end, a point of inflection at a concentration of about 0.4 molal, and a slight positive curvature at the upper end. These deviations from linearity are apparent from Col. 3 of Table III, which gives the values of $(\eta - 1)/c$, which would be a constant if the line were straight. These values are plotted in Fig. 1, Curve C. We next tested the Arrhenius equation, $\eta = A^c$, or $\log \eta = c \log A$. If this equation holds, $(\log \eta)/c$ should be a constant, but it is evident from Col. 4 that $(\log \eta)/c$ is by no means a constant, especially at low concentrations, so that the Arrhenius equation must be rejected. Bingham[18] has pointed out that in the case of mixtures of organic liquids the relationships are simpler if the computation or curves, instead of being based on viscosity, are based on its reciprocal—the fluidity. This suggested that we try the fluidity in the case of aqueous solutions of electrolytes. Column 5 gives the fluidity, φ, at each concentration and Col. 6 the value of $(\varphi - 1)/c$. As will be seen, these values are by no means constant, showing that the fluidity is not a linear function of the concentration. Although the fluidity–concentration curve has a positive curvature at the dilute end (corresponding to the negative curvature of the viscosity–concentration curve) it has no point of inflection and no double curvature (up to 1 molal at least), and therefore evidently has a simpler form than the viscosity-concentration curve.

It was evident from our study of our data reinforced by data on other salts by Grüneisen, Applebey, and Merton that, although the principal effect of dissolved salts on viscosity or fluidity is proportional to the concentration, there must be some effect which is of relatively greater importance in dilute solutions and which is responsible for the curvature found in the dilute end of the viscosity–concentration and of the fluidity–concentration curves. Furthermore, this effect always tends to increase the viscosity regardless of whether the sum of all of the effects of adding the salt is an increase or decrease of the viscosity. The interionic attraction theory of

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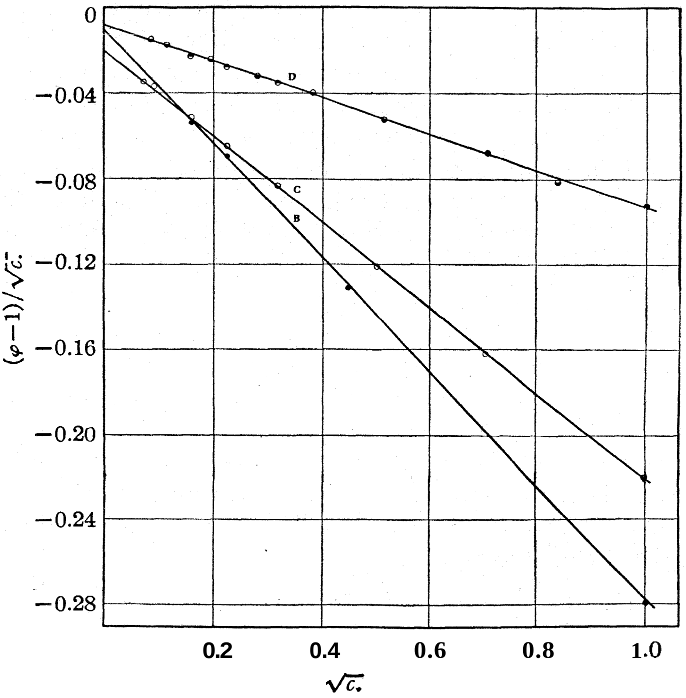
[18] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Company, Inc., New York, 1922, Part II, Chapter I.

electrolytes gives a clue to the nature of this effect. According to this theory the ions tend to build and maintain a space lattice structure in the solution and any influence tending to disturb this space lattice arrangement whether by heat motion of the solvent molecules, the electrostatic force of charged electrodes in the solution, or any relative motion of parts of the liquid, will be opposed by the interionic forces. The forces which tend to maintain a space lattice structure of the ions, therefore, tend to stiffen the solution or increase its viscosity.[19] The effect of the interionic forces in opposing the motion of ions in an electric field has been shown by Debye and Hiickel to be proportional to the square root of the concentration in very dilute solutions. It therefore occurred to us to try introducing a term proportional to the square root of the concentration into the equation for the fluidity, giving an equation of the form



Curve D, $LiNo_3$ at 18°, ○ Applebey, ● Griineisen; C, $BaCl_2$ at 25°, Jones and Dole; B, $LiIO_3$ at 18°, Griineisen.

Fig. 2.—$(\varphi-1)/\sqrt{c}$ against $\sqrt{c}$.

$$\varphi = 1 + A\sqrt{c} + Bc$$

Since the interionic forces mentioned above tend to stiffen the solution or decrease its fluidity, it is to be expected that A will have a negative value

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[19] W. Sutherland, *Phil. Mag.*, [6] 14, 1 (1907), suggests that interionic attraction should increase the viscosity.

for all strong electrolytes and the value 0 for non-electrolytes. Whether B will be positive or negative for any particular salt can only be determined at present by a study of the experimental data. Thus B will be positive for salts like potassium iodide or cesium nitrate which increase the fluidity and negative for salts which, like barium chloride, diminish the fluidity. This equation may readily be transformed to the form $(\varphi - 1)/\sqrt{c} = A + B\sqrt{c}$. Therefore, the simplest way to test the validity of this equation is to plot $(\varphi - 1)/\sqrt{c}$ against $\sqrt{c}$ and see if a straight line is obtained which does not pass through the origin. This was done with our data on barium chloride and gave a good straight line through the entire range from **0.005** to **1.0** molal. This curve (C) is reproduced on a much reduced scale in Fig. 2. It will be noticed that the intercept on the $(\varphi - 1)/\sqrt{c}$ axis, which gives the value of A, is negative, as was predicted, and that the slope, which gives the value of B, is also negative in this case. The numerical values of A and B were then determined with greater precision than is possible by plotting by the method of least squares, giving

$$\varphi = 1 - 0.02013\sqrt{c} - 0.20087\sim$$

The values of the fluidity as computed by this equation are shown in Col. 7 of Table III and the deviations between the computed and observed values in Col. 8. The greatest deviation is only **0.032%** and the average deviation only 0.013% and there is no systematic trend. It may be concluded, therefore, that this equation is valid for barium chloride solutions at 25° within the limit of accuracy of the experiments over the entire range up to 1 molal. Table IV gives the values of φ and η at round concentrations computed from this equation.

TABLE III

VISCOSITY AND FLUIDITY OF BARIUM CHLORIDE SOLUTIONS AT 25°

c	η	$(\eta - 1)/c$	$(\log \eta)/c$	$\varphi_{obs.}$	$(\varphi - 1)/c$	$\varphi_{comp.}$	$\Delta\varphi$, obs.-comp.
0.005	1.00248	0.496	0.215	0.99753	−0.494	0.99757	−0.00004
.01	1.00371	.371	.161	.99630	− .370	.99598	+ .00032
.025	1.00821	.328	.140	.99186	− .326	.99180	+ .00006
.05	1.01474	.295	.127	.98547	− .291	.98546	+ .00001
.1	1.02704	.270	.116	.97367	− .263	.97355	+ .00012
.25	1.06438	.258	.108	.93951	− .242	,93973	− .00022
,4972	1.12893	.259	.105	.88579	− .230	.88594	− .00015
.9913	'1.28049	.283	.108	.78095	− .221	.87084	+ .00011

TABLE IV

FLUIDITY AND VISCOSITY OF BARIUM CHLORIDE SOLUTIONS AT 25°

c	0.0005	0.001	0.0025	0.005	0.01	0.025
φ	0.99945	0.99916	0.99843	0.99757	0.99598	0.99180
η	1.00055	1.00084	1.00157	1.00244	1.00404	1.00827

c	0.05	0.10	0.25	0.50	1.0
φ	0.98546	0.97355	0.93973	0.88533	0.77900
η	1.01475	1.02717	1.06414	1.12952	1.28370

TABLE V

VISCOSITY AND FLUIDITY OF LITHIUM NITRATE SOLUTIONS AT 18° AFTER GRÜNEISEN (G) AND APPLEBEY (A)

	c	η	$(\eta - 1)/c$	$(\log \eta)/c$	$\varphi_{\text{obs.}}$	$(\varphi - 1)/c$	$\varphi_{\text{comp.}}$	$\Delta\varphi$, obs.-comp
A	0.00724	1.0012$_5$	0.173	0.0749	0.99875	−0.173	0.99869	+0.0000$_6$
A	.01310	1.0020$_1$	.153	.0666	.99799	− .152	.99796	+ .0000$_3$
G	.02500	1.00364	.146	.0631	.99637	− .145	.99659	− .0002$_2$
A	.0379	1.0047	.124	.0537	.99532	− .123	.99520	+ .0001$_2$
G	.0500	1.00622	.124	.0538	.99382	− .123	.99394	− .0000$_8$
A	.0784	1.0090	.115	.0496	.99108	− .114	.99108	+ .0000$_0$
G	.1000	1.0112	.112	.0483	.98889	− .111	.98895	− .0000$_6$
A	.1446	1.01535	.106	.0457	.98488	− .104	.98466	+ .0002$_2$
A	.2653	1.0276	.104	.0446	.97314	− .101	.97335	− .0002$_1$
G	.5000	1.05032	.101	.0426	.95209	− .096	.95193	+ .0001$_6$
A	(.7034)	(1.0731)	(.104)	(.0434)	(.93188)	(− .097)	(.93365)	(− .0017$_7$)
G	1.000	1.1023	.102	.0423	.90719	− .093	.90724	− .0000$_5$
A	1.283	1.1429	.111	.0452	.87497	− .097	.88222	− .0072$_5$
A	1.471	1.16865	.115	.0460	.85569	− .098	.86566	− .0099$_7$
A	2.528	1.3472	.137	.0512	.74228	− .102	.77417	− .0318$_9$
A	2.550	1.3552	.139	.0517	.73790	− .103	.77126	− .0333$_6$
A	3.120	1.48695	.156	.0553	.67252	− .105	.72167	− .0491$_5$
A	3.279	1.5327	.162	.0565	.65244	− .106	.70785	− .0554$_1$
A	4.363	1.9274	.213	.0652	.51883	− .110	.61390	− .0950$_7$

Analysis and Interpretation of Other Data.—Most of the data in the literature are not well suited to test the generality of our new relationship because measurements on very dilute solutions are lacking. Most authors have apparently assumed that at low concentrations the curves become linear. The best available data for this purpose known to us are those of Grüneisen and of Applebey on lithium nitrate at 18° which cover the range from 0.00724 to 4.363 moles per liter. These data were first used to prepare a plot of $(\varphi - 1)/\sqrt{c}$ against $\sqrt{c}$ and gave a good straight line up to 1 molal, which is reproduced in Curve D of Fig. 2, giving negative values of A and B, as was expected. Then the equation of this line was determined by the method of least squares. (In this computation the data for Applebey's 0.7034 molal solution were omitted because the plotting indicated a serious error in this value.) The result was

$$\varphi = 1 - 0.00818\sqrt{c} - 0.08458c$$

The fundamental data and the derived values are shown in Table V. The conclusion that Arrhenius' equation is invalid is reinforced by a consideration of Col. 4. As will be seen by inspection of Col. 8, the values of the fluidity computed by our formula agree with the experimental results within 0.022% for all solutions measured up to 1 molal except for Applebey's 0.7034 molal solution, which is apparently in error experimentally. These data on lithium nitrate confirm in all respects the conclusions which we have drawn from our own data on barium chloride.

Grüneisen's data on lithium iodate have been used to prepare Curve B in Fig. 2. Lithium iodate solutions have an exceptionally high viscosity, but in spite of the magnitude of the effect, the equation

$$\varphi = 1 - 0.01076\sqrt{c} - 0.2689{\sim}$$

is in accord with the data up to 1 molal with a maximum deviation of only 0.03%. The equation, however, fails completely at 3 molal.

We have plotted the data on a number of other salts which increase the viscosity of water but forego to adduce other examples since in all other cases known to us the measurements lack precision or there are not sufficient measurements on solutions of low concentration to permit a sharp test of the validity of our general equation. The evidence of other cases studied, however, so far as it goes, supports the validity of our equation.

We next turn to salts which may decrease the viscosity of water within certain ranges of concentration and temperature. Such salts are sometimes said to exhibit a "negative viscosity" but this is not accurate phraseology since there is no such thing as a negative viscosity. Here the phenomena are more complicated than for salts which increase the viscosity. The data which are most suitable for testing our equation are the measurements of Merton[11] on cesium nitrate. Merton has made accurate measurements at 0° covering the range 0.025 to 0.42 molal, at 10° covering the range 0.029 to 0.7, at 18° covering the range 0.023 to 0.8, and at 25° covering the range 0.023 to 0.8. The values of $(\varphi - 1)/\sqrt{c}$ were plotted against $\sqrt{c}$. The resulting plots, which are omitted to save space, appear to be straight lines at the dilute end (below 0.2) but deviations are evident at higher concentrations; whereas for the salts which increase the viscosity, the straight lines were obtained up to 1 molal in the cases studied.

It is evident from these curves that the value of A is always negative, as is expected from our theoretical interpretation of the phenomena. Then by the method of least squares the coefficients were determined, giving at 18°

$$\varphi = 1 - 0.01029\sqrt{c} + 0.12456{\sim}$$

and at 0°

$$\varphi = 1 - 0.01488\sqrt{c} + 0.2587{\sim}$$

These data furnish further evidence as to the invalidity of Arrhenius' formula. There are several inferences which may be drawn tentatively from the variation of the constants with the temperature although we must be cautious because the available data do not extend to solutions as dilute as is desirable for the evaluation of the constant A. However, there are indications that the numerical value of A is greater at low temperatures than at high temperatures. Since A depends upon the stiffening effect of the space lattice, it is to be expected that this effect will be greater at low temperatures because the space lattice is less disturbed by heat vibration. This effect apparently exceeds the opposite effect of the change in dielectric constant with temperature. It is also to be observed that the value of B is greater at low temperatures, which is in harmony with Applebey's suggestion that the increase in fluidity is due to depolymerization of triple water molecules. There are more triple molecules present at low temperatures and therefore more available to be depolymerized.

Grüneisen's data on potassium iodide and potassium nitrate at 18° have been computed and plotted and found to fit an equation of the same form with a negative value of A up to 0.2 molar.

If our hypothesis that the negative curvature at the lower end of the viscosity–concentration curves is due to a stiffening effect of the ionic space lattice is correct, there should be no such negative curvature manifested in solutions of non-electrolytes. Accurate measurements of the viscosity of such solutions at very low concentrations are very scarce in the literature. The best examples known to us are the data of Grüneisen on sucrose and of Washburn and Williams[20] on raffinose at three temperatures. Grüneisen's measurements extend down to 0.01 molal and according to Grüneisen may be accurately represented by the equation

$$\eta = 1 + 0.8816c + 0.7970c^2$$

and thus show no evidence of negative curvature at low concentrations or of any influence which is proportional to the square root of the concentration. The measurements of Washburn and Williams on raffinose extend down to 0.038 molal and also give no indication of a negative curvature at the dilute end of the viscosity-concentration curves. Further corroboration is given by the measurements of Chadwell[21] on aqueous solutions of methyl acetate, ethyl acetate and diethyl ether, which, although not extending to as great dilution as would be desirable to test this question, nevertheless show no indication of a negative curvature at the dilute end of the viscosity–concentration curves.

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 concentration will give an increase in viscosity at extreme dilutions is by Schneider,[9] who reports a relative viscosity of 1.0008 for 0.05 N potassium chlorate, and 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.

Grateful acknowledgment is made to Professor Theodore Lyman, Director of the Jefferson Physical Laboratory, for permission to work in that Laboratory and for making available to us its standard clock. We also wish to express our appreciation for a grant from the Milton Fund of Harvard University for the expenses of this research.

[20] E. W. Washburn and G. T. Williams, THIS JOURNAL, 35, 750 (1913).

[21] H. M. Chadwell, ibid., 48, 1912 (1926).

Summary

1. Measurements have been made on the viscosity of solutions of barium chloride at 25° covering the range 0.005 to 1.0 molal.

2. The fluidity (reciprocal of the viscosity) of these solutions can be computed within the limit of error of the data from the equation

$$\varphi = 1 - 0.02013\sqrt{c} - 0.20087c$$

3. It is shown that an equation of the form $\varphi = 1 + A\sqrt{c} + Bc$ can be made to fit the data by proper choice of the values of A and B in the case of many other salts for which precise data are available extending to low concentrations.

4. The value of A is negative for all strong electrolytes for which accurate data are available. This term probably represents the stiffening effect on the solution of the electric forces between the ions which tend to maintain a space lattice structure. The value of A is zero for non-electrolytes.

5. The value of B may be either positive or negative. Most salts resemble barium chloride in causing an increase in viscosity or a decrease in fluidity at all concentrations giving a negative value to B. In such cases the equation is apparently valid up to about 1 molal.

6. Some salts cause an increase in the fluidity or a decrease in the viscosity over a wide range of concentration, so that the value of B in our equation is positive. In such cases the equation is apparently valid up to nearly 0.2 molal.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, MICHIGAN AGRICULTURAL EXPERIMENT STATION]

THE DETERMINATION OF ALUMINUM IN PLANTS. II. ALUMINUM IN PLANT MATERIALS[1]

BY O. B. WINTER AND O. D. BIRD

RECEIVED JUNE 12, 1929 PUBLISHED OCTOBER 5, 1929

The biological significance of the use of aluminum in food materials, water purification, cooking utensils, etc., has been a live problem during the last one or two decades. Because of this, the aluminum content of plants has been considered of importance, even though the amount present may be small.

Langworthy and Austin,[2] Gonnerman,[3] Bertrand[4] and more recently

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[1] Published by permission of the Director of the Experiment Station as Journal Article No. 11 n.s. from the Station and No. 49 from the Chemical Laboratory.

[2] Langworthy and Austin, "The Occurrence of Aluminum in Vegetable Products, Animal Products and Natural Waters," New York, 1904.

[3] Gonnerman, *Biochem. Z.*, **88**, 401 (1918).

[4] Bertrand, *Bull. soc. hyg. aliment.*, **8**, 49 (1920).

Myers and Voegtlin,[5] Gray,[6] McCollum, Rask and Becker,[7] and others have made quantitative determinations of aluminum in plant materials. All of these analysts, with the exception of McCollum, Rask and Becker, found aluminum present in these materials. The differences in the results obtained by these analysts, however, indicate that there is considerable variation in the aluminum content of some of the materials analyzed or that some of the materials were contaminated more than others. Because of these variations and because of the present interest in the aluminum content of foods, a number of plants and plant materials were analyzed for this element by the colorimetric method[8] described in an earlier article. The work herein presented gives the method used for preparing the samples for analysis and also the results of aluminum determinations.

Experimental Part

Preparation of the Material.—Since the real problem at hand was to determine the amount of aluminum in the materials as they are used for food, the samples were prepared in practically the same way as in the ordinary preparation for table use. The impurities were removed when possible by carefully washing the materials with water and a brush. When the impurities were not readily removed by this method, as in the case of some roots, the contaminated spots were scraped with a knife and then washed. All fresh materials were dried at approximately 35°. The moisture was determined. The dry materials were ground so as to pass a 20-mesh sieve and stored in stoppered bottles.

Preparation of the Sample.—From 1 to 30 g. of material (depending on the amount of aluminum present) was placed in a platinum dish in an electric muffle, the temperature was raised to just below redness and allowed to remain overnight. Any unburned carbon at this point was ignored, since it could be ignited later. The ash was digested with hydrochloric acid, centrifuged, the supernatant liquid decanted and the residue washed once with about 5 cc. of water by means of the centrifuge and decantation. Since it was found that the aluminum in the ash was not always entirely dissolved by hydrochloric acid, the residue was washed into a platinum crucible by means of a fine jet of water, the water evaporated, the residue ignited if necessary, fused with 0.5 g. each of sodium and potassium carbonates, taken up with hydrochloric acid and added to the original solution.[9]

Determination of Aluminum.—After adding a few drops of nitric acid and boiling to oxidize the iron and removing the silica by dehydration, the solution was transferred to a centrifuge tube of about 25-cc. capacity with marks at 15.20 and 25 cc. The iron

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[5] Myers and Voegtlin, "U. S. Weekly Public Health Rep. 29," Part 1, Nos. 1–26, 1625 (1914).

[6] Gray, Hearings, Dochet 540, U. S. Federal Trade Commission *vs.* Royal Baking Powder Co.

[7] McCollum, Rask and Becker. *J. Biol. Chem.*, 77, 753 (1928).

[8] Winter, Thrun and Bird, THIS JOURNAL, 51, 2721 (1929).

[9] The wet method (digesting the sample with sulfuric and perchloric acids) used by Myers and co-workers was tried. The method proved entirely satisfactory when only a comparatively small sample was used, *e. g.*, 1 g. However, since the blank on the reagents was appreciable, in cases where only a small amount of aluminum was present, it was found much more satisfactory to ash a larger sample, carry it through to where the iron is separated and then take an aliquot of the solution.

and aluminum were precipitated and the iron was separated by the method of Myers. Mull and Morrison[10] (practically all of the materials analyzed contained sufficient iron to carry down the aluminum but did not contain phosphoric acid enough to insure complete precipitation of the iron and aluminum as phosphates; hence no iron but about 0.10 g. of ammonium hydrogen phosphate was added to each sample). The solution was made up to a volume of 25 cc. An aliquot was transferred to a 50-cc. volumetric flask, a small piece of litmus paper was added, then water to make a volume of about 20 cc., and finally hydrochloric acid until the litmus paper just turned red. The aluminum was determined by the colorimetric method previously mentioned.

The Blank.—Among the reagents used for making aluminum determinations, sodium hydroxide, sodium carbonate and potassium carbonate contain aluminum. Ordinary C. P. sodium hydroxide is not suitable for this work, but samples specially prepared from metallic sodium were obtained which contained very little of the element. The carbonates contained only a very small amount. In every case, however, it was found necessary to run a blank on all the reagents used and make a correction.

Comparison of Methods.—In order to check the method herein used for making aluminum determinations, the combined iron and aluminum were determined in each of three plant materials by the method described by Patten and Winter.[11] The iron was also determined colorimetrically by the method described in the same paper and the aluminum by the method herein referred to. The results of this work are found in Table I.

TABLE I

COMPARISON OF METHODS

Sample	$FePO_4 + AlPO_4$, %	Fe, %	Al, %	Calcd. to $FePO_4 + AlPO_4$, %
1	1.530	0.250	0.141	1.514
2	0.800	.104	.098	0.737
3	.860	.126	.107	.860

The data in Table I indicate that the method herein described gives fairly accurate results.

The Recovery of Aluminum Added to Materials.—In order to show whether or not the aluminum added to materials can be determined, different quantities of aluminum chloride solution were added to four samples of red beets. The samples were ashed and the aluminum was determined. The results are shown in Table II.

TABLE II

RECOVERY OF ALUMINUM

Material	Sample	S. + 0.01 mg. Al	S. + 0.02 mg. Al	S. + 0.03 mg. Al
Al found, mg.	0.0038	0.0130	0.0230	0.0325

These results indicate that added aluminum can be accurately determined.

Table III gives a list of plant materials on which aluminum determinations were made. Tap water and a few animal products used for food are

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[10] Meyers, Mull and Morrison, J. *Biol. Chem.*, 78, 595 (1928).

[11] Patten and Winter, J. Am. Off. Agr. Chem., 11, 202 (1928).

also included. Where the materials were sufficiently dry to be readily mixed and ground the results are expressed in parts per million of aluminum in the dry sample; otherwise the percentage of water and the parts per million of aluminum in the wet sample are also given. (In making these determinations corrections were made for all of the reagents used.)

The data in Table III show that aluminum was found in all of the

TABLE III

ALUMINUM IN PLANT AND ANIMAL MATERIALS

Materials	H_2O, %	Al, p.p.m. Dry	Al, p.p.m. Wet
Apples	87	8.4	1.1
Asparagus	93	50.0	3.5
Alfalfa hay	..	99.0	..
Banana peels	87	26.9	3.5
Barley	..	11.3	..
Beans, green string	90	50.0	5.0
Beans, yellow string	91	101.1	9.1
Beans, light red kidney	..	7.0	..
Beans, dark red kidney	..	14.5	..
Beans, early prolific	..	9.0	..
Beans, pea	..	10.5	..
Beans, sulfur	..	7.0	..
Beef, dried	54	30.2	13.9
Blood, dried	..	8.5	..
Beets	86	26.4	3.7
Beets	85	12.7	1.9
Beet tops	92	293.8	23.5
Cabbage	93	32.9	2.3
Carrots	89	90.9	10.0
Carrots	91	28.9	2.6
Carrots	86	20.7	2.9
Carrots	91	22.2	2.0
Carrot tops	81	214.2	40.7
Cauliflower	89	66.4	7.3
Celery	94	58.3	3.5
Corn flakes	..	2.8	..
Corn, flint	..	2.1	..
Corn, popcorn	..	4.0	..
Cucumbers	96	67.5	2.7
Dates (pulp)	17.5	12.9	10.7
Dates (pits)	10	11.1	10.0
Eggs, dried	..	12.0	..
Eggs, dried	..	12.4	..
Figs	20	23.0	18.4
Fish, cod	60	7.8	3.1
Fish, white	81	15.8	3.0
Fish, herring	20	11.0	8.8
Grape fruit	88	7.5	0.9.
Kohlrabi	92	27.5	2.2
Lemons	84	9.4	1.5
Lettuce (roots)	85	850.0	127.5
Lettuce (tops)	92	155.0	12.4
Lettuce (whole)	88	246 7	29.6
Linseed meal	..	73.0	..
Mustard seed	..	67.0	..
Milk, dried skim	..	4.0	..
Milk, dried buttermilk	..	28.0	..
Milk, dried buttermilk	..	21.2	..
Oatmeal	..	15.1	..
Oranges	83	9.4	1.6
Parsnips	80	21.0	4.2
Parsnips	82	23 3	4 2
Parsnips	83	14 1	2 4
Peanut meats	..	7.6	..
Peanut shells	..	325.0	..
Pecan meats	..	4 2	..
Peas, green	78	11.4	2.5
Peas, yellow	..	5.8	..
Peas, white	..	8.8	..
Potatoes	80	11.0	2.2
Prunes (pulp)	24	20.5	15.6
Prunes (pits)	14.5	7.6	6.5
Radishes	94	80.0	4.8
Raisins	17.5	20.4	16.9
Raisins	17.5	24.2	20.0
Rice	..	4.7	..
Rhubarb (stems)	97	63.3	1.9
Rhubarb (leaves)	93	34.3	2.4
Strawberries	93	44.5	3.1
Walnut meats (Eng.)	..	5.0	..
Walnut shells (Eng.)	..	22.0	..
Water, tap	..	..	0.04
Wheat	..	4.5	..
Wheatbran	..	6.0	..
Wheat middlings	..	3.3	..
Wheatflour	..	2.0	..

materials analyzed in quantities ranging from 2.0 p.p.m. in wheat flour to 325.0 p.p.m. in peanut shells. It should be noted here that in all cases where the aluminum content ran unusually high (peanut shells, lettuce, carrot tops, beet tops, etc.) the sample was of such material that the adhering impurities could not be completely removed.

Since in the analyses made of the materials in Table III no special precautions were taken to remove the outer surfaces which undoubtedly were contaminated, samples of four different materials were cleaned and pared so as to remove all of the exterior portions. These were carefully dried, ground in an iron mortar and analyzed for aluminum. The results of these analyses and four blanks which were run at the same time are shown in Table IV.

TABLE IV

ALUMINUM IN FOUR SPECIALLY PREPARED MATERIALS

Material	Sample, g.	Aluminum Mg.	Aluminum P.p.m. corr. for blank
Apples	1.00	0.0145	5.2
Red beets	2.50	.0240	5.9
Potatoes	2.50	.0197	4.2
Carrots	1.25	.0379	22.8
Blanks		0.0090 0.0098	
		0.0083 0.0102	
	Av.	.0093	

The results in Table IV show that aluminum was found present in each of the materials analyzed or that some other element was present which reacted like aluminum with the dye. Since all elements known to interfere with this reaction had been removed, we conclude that aluminum was a constituent of these materials.

Summary and Conclusions

1. A method is given for the preparation of plant materials for making colorimetric aluminum determinations.
2. The results of determinations of aluminum in 76 samples of materials are presented.
3. Aluminum was found present in all of the samples examined.
4. Four samples which were carefully prepared by removing the external surfaces so as to avoid contamination were analyzed and aluminum was found present in each of them.

EAST LANSING, MICHIGAN

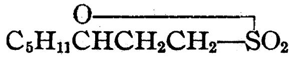
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE STANDARD OIL DEVELOPMENT COMPANY]

A NEW PETROLEUM BY-PRODUCT: OCTANESULTONE

BY E. L. BALDESCHWIELER AND H. A. CASSAR

RECEIVED OCTOBER 27, 1928 PUBLISHED OCTOBER 6, 1929

In the process for the manufacture of the higher secondary and tertiary alcohols such as isopropyl, secondary butyl, amyl and hexyl alcohols, etc., as used in the alcohol plant of the Bayway Refinery of the Standard Oil Company of New Jersey, the permanent gases from the stills are scrubbed first through a strong solution of sulfuric acid. The unsaturated compounds such as olefins are thus extracted by the acid. The latter is then diluted with water and hydrolysis takes place with the separation on the surface of a dark liquid of a very disagreeable odor and of high sulfur content. The latter is then drawn off and on cooling and standing deposits a black material. From this substance a new compound has been separated by extraction with hot benzol and precipitation with gasoline, whereupon a large crop of crystals was obtained which were found to consist of a single compound of the empirical formula $C_8H_{16}SO_3$ melting at 129.[1]

Structural **Formula.**—The structural formula  $C_5H_{11}\overset{O}{C}HCH_2CH_2\text{—}SO_2$ was assigned to this compound from the data and deductions given below,

The empirical formula is $C_8H_{16}SO_3$, and molecular weight determinations show the compound to be monomolecular.

The compound does not form salts with dilute alkalies in the cold and reacts neutral to indicators; therefore it does not contain a free acid group.

The compound reacts acid on boiling with water; therefore it must contain an acid group bound up with an hydroxyl group, since the compound does not contain nitrogen.

The compound gives no bromine number and so does not contain an unprotected double bond; it cannot be brominated in a boiling solution of acetic acid and sodium acetate, and therefore can scarcely contain an aromatic nucleus.

The compound is not attacked by boiling acetyl chloride and hence can scarcely contain any free hydroxyl groups.

The compound on heating with dilute sulfuric acid under pressure and also on distillation over caustic potash liberates sulfur dioxide and yields a number of isomeric octanes and octenes boiling mainly around 110 to 116°; this splitting off of sulfur dioxide is characteristic of sulfonic acids.

On refluxing the compound with barium hydroxide a barium salt is obtained, the analysis of which agrees with the formula

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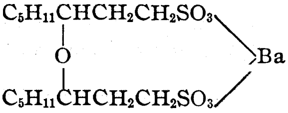
[1] The compound was isolated by E. L. Baldeschwieler, who first purified it and determined its empirical formula and physical constants; the chemical properties and structure were worked out by H. A. Cassar.



This formula represents the anhydride of the barium salt of an hydroxyoctanesulfonic acid. All attempts to prepare the hydrated compound failed; the silver salt was prepared by double decomposition from the barium salt and the potassium salt from the original compound by means of potassium hydroxide. These salts were found to be anhydrides, too, and were prepared to determine whether the double valency of the barium atom might have had any effect in promoting closure of the ring with elimination of the elements of water; this effect was not observed to take place.

In a further search for the hydrated salt hydrolysis with mild alkalies was tried, but sodium carbonate yields the same salt, and barium carbonate yields a crystalline salt which is also anhydrous and a sirup, both of which derivatives were proved to be different from the salt by barium hydroxide.

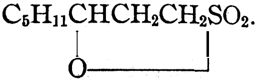
The simplest member of the oxysulfonic acids is oxyethanesulfonic acid (isathionic acid), $HOCH_2CH_2SO_3H$, and when the barium salt of this acid is heated to 190 it loses the elements of water and changes into di-isathionic acid (di-ethyl ether β,β'-disulfonic acid).[2] It is not surprising, therefore, that when dealing with a higher member of this series containing eight carbon atoms the anhydrides should be the compound obtained, as the stability of organic compounds diminishes with increase in the length of the carbon chain, and anhydrides are generally more stable than hydrates.

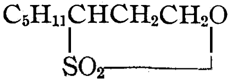
When the barium salt by barium hydroxide or the sirup by barium carbonate are treated with dilute mineral acids and refluxed, the original compound separates out.

This hydrolysis by means of dilute alkalies and reformation by means of acids is characteristic of carboxylic and sulfonic acid lactones; the great solubility of the alkaline salts incidentally excludes carboxylic acids altogether.

All that remains now is to determine whether the amyl grouping in the compound is a straight or a branched chain and to characterize it. Unfortunately this point is still obscure. The main difficulty is the lack of intermediate compounds such as amyl- and hexyl halides and olefins of known constitution and well-defined methods for identifying them in small quantities, which makes the remaining part of the problem almost hopeless of solution at the present time.

Since we are dealing with a sulfonic acid lactone with an octane group in it, and since all sulfonic acid lactones so far prepared in the aromatic series are γ-lactones, we must have a compound of the structure $C_5H_{11}\underset{\llcorner O}{C}HCH_2CH_2\underset{\lrcorner}{SO_2}$. The structure $C_5H_{11}\underset{\llcorner SO_2}{C}HCH_2CH_2\underset{\lrcorner}{O}$ is highly im-





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[2] Carl, *Ber.*, 14, 65 (1881).

probable since primary alcohols are known not to form sulfonic lactones (see below) and also all alcohols made from olefins and sulfuric acid are secondary or tertiary. This compound we propose to call octane-sultone to fall in line with the present accepted nomenclature in the aromatic series.

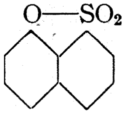
Naphthsultone,  , discovered by C. Mensching, examined by G. Schultz[3] and further investigated by H. Erdmann,[4] who invented the name sultone for this class of compound, contains three carbon atoms in the lactone group and is, therefore, a γ-sulfonic lactone. Ortho-phenol sulfonic acid, which could only give a β-sulfonic lactone, does not form a ring compound at all, but o-benzyl alcohol sulfonic acid forms a γ-sulfonic lactone called benzyl-sultone by the discoverers, W. Marckwald and H. H. Frahne.[5] All this leads one to expect the present sultone to be gamma; $CH_2OHCH_2CH_2SO_3H$ was also prepared by the latter co-workers and no lactone could be prepared from it, probably because the hydroxyl group is a primary alcohol.

TABLE I

SOLUBILITIES

	Octane-sultone	Benzyl-sultone	Naphthsultone
Cold water	Slight	Slight	?
Hot water	Medium	Medium	?
Cold alcohol	Slight	Slight	Slight
Hot alcohol	Very	Very	?
Chloroform, hot and cold	Very	Very	Very
Hot benzol	Very	Very	Very
Ligroin	Very slight	Very slight	?

Both octane-sultone and naphthsultone give flat transparent glassy crystals on slowly evaporating their benzol solutions, and all three can be sublimed; octane-sultone and benzyl-sultone are volatile in steam and naphthsultone distils unchanged.

All three sultones are dissolved by hot but not cold strong alkali, and the free acids of naphthsultone and benzyl-sultone are stable and are only changed back into the sultones by such drastic treatment as sublimation or phosphorus pentachloride, while octane-sultone changes from the free acid into the sultone by standing in warm dilute acid solutions overnight. Naphthsultone is not dissolved by alkali carbonates while octane-sultone is. As can be seen from the above comparison, the general properties of the three sultones are very similar.

Halogenation.—Octane-sultone cannot be brominated, but its alkaline salts, of which there are three varieties, absorb bromine very rapidly in

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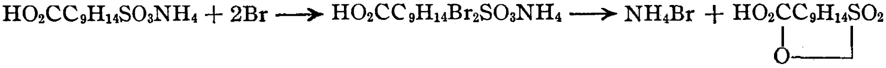
[3] Schultz, *Ber.*, 20, 3162 (1887).

[4] Erdmann, Ann., 247,344 (1888).

[5] Marckwald and Frahne, *Ber.*, 31,1898 (1898).

alkaline solution with reformation of the sultone ring. This is scarcely odd, since Géza Braun, for instance, found that the lactone of hydroxyisocrotonic acid had maximum ability to absorb bromine only immediately after saponification.[6] Also, when ammonium hydrogen sulfocampholenecarboxylate is treated with bromine in aqueous solution, a white precipitate of the brominated sultone is thrown down.[7]



$$HO_2CC_9H_{14}SO_3NH_4 + 2Br \longrightarrow HO_2CC_9H_{14}Br_2SO_3NH_4 \longrightarrow NH_4Br + HO_2CC_9H_{14}SO_2$$

Type A salt, obtained by hydrolysis of the sultone with barium or calcium hydroxide, with sodium or potassium hydroxide and with sodium or potassium carbonate, absorbs two atoms of halogen in aqueous solution, yielding a monohalogen derivative with immediate reformation of the sultone ring. The position of the halogen atom is unknown but it is probably adjacent to the sulfonic group. On refluxing these halogenated octanesultones with strong alkali, they hydrolyze to easily crystallizable salts of oxyhalogenoctanesulfonic acids; the halogen atom is not hydrolyzed off, even on fusion with caustic soda. All attempts to reduce the halogen atom failed; a zinc–copper couple is sufficiently alkaline to yield the zinc salt of the oxyhalogenoctanesulfonicacid. The free acid was prepared from the barium salt through the lead salt followed by hydrogen sulfide and was found to be extremely soluble in water and not to show any tendency to reform the sultone. It is probable that the halogen atom is next to the sulfonic group, the sulfonic group hindering the hydrolysis and reduction of the halogen group, and the halogen group hindering the ring-closing tendency of the sulfonic group.

Type B salt, obtained by hydrolyzing the sultone with barium carbonate, is a sirup, and absorbs halogens like those of Type A, yielding monohalogen derivatives with immediate reformation of the sultone ring. These halogenated sultones of Type B are isomeric with those of Type A, but either strong or mild alkali splits off the halogen atom as halogen acid and at the same time hydrolyzes the sultone ring to give a salt that cannot be crystallized. On treating this sirup with warm dilute mineral acids the unsaturated sultone is obtained that crystallizes from dilute alcohol in beautiful white needles.

Here too the double bond and hence the original halogen atom must be in close juxtaposition with the sulfonic group, probably in the β-position with respect to it as the unsaturated sultone, which does not absorb bromine in the ring form, absorbs one atom of halogen by displacement in the form of its alkaline salts to give an unsaturated halogenated octane-sultone; here too the sultone ring is reformed at the instant of halogenation.

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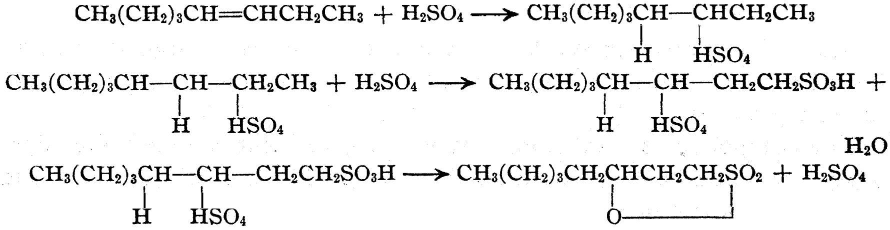
[6] Braun, THIS JOURNAL, **51**, 241 (1929).

[7] Harvey and Lapworth, J. Chem. *Soc.*, **83**, 1102 (1903).

Enough is already known about unsaturated sulfonic acids in the aliphatic series to make this reaction seem plausible; for ethylene sulfonic acid absorbs bromine by substitution and not by addition.[8]

Type C salt, obtained by hydrolyzing the sultone with excess barium or calcium carbonate, is easily crystallized; it is completely isomeric with salts of Type A, being also the salt of an anhydride; treating this salt with warm dilute mineral acids does not give back the original sultone as with Types A and B but the sulfonic group is split off and an olefin boiling at i13 to 115° is obtained. Also, on halogenation the sulfonic group is split off and a mixture of octane mono and di-halides is the result. On treating salts of Type C with free iodine in warm aqueous solution alkyl iodides are obtained which decompose readily on steam distillation to olefins, which indicates that these alkyl halides are secondary or tertiary derivatives, since primary iodides as a rule can be steam distilled.

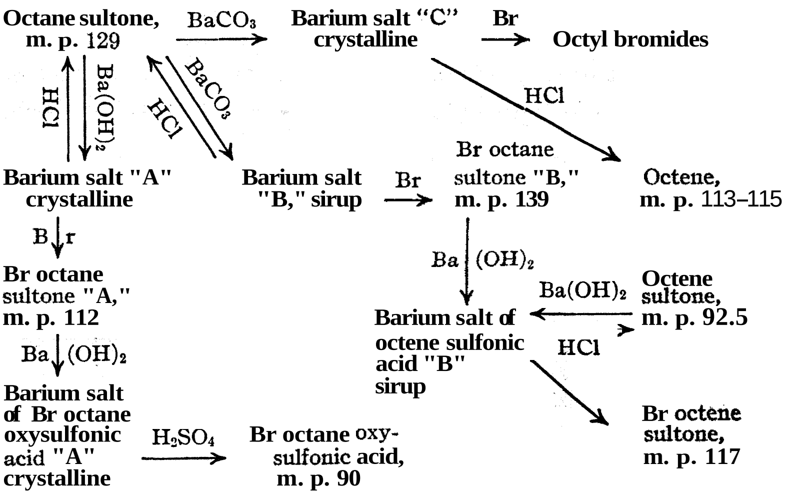
Octane-sultone, unlike carboxylate lactones, is not attacked by phosphorus pentachloride or acetyl chloride; the alkaline salts Types A and B are decomposed by the former and changed back by the latter into the original sultone.



$$CH_3(CH_2)_3CH{=}CHCH_2CH_3 + H_2SO_4 \longrightarrow CH_3(CH_2)_3\underset{H}{CH}{-}\underset{HSO_4}{CH}CH_2CH_3$$

$$CH_3(CH_2)_3\underset{H}{CH}{-}\underset{HSO_4}{CH}{-}CH_2CH_3 + H_2SO_4 \longrightarrow CH_3(CH_2)_3\underset{H}{CH}{-}\underset{HSO_4}{CH}{-}CH_2CH_2SO_3H + H_2O$$

$$CH_3(CH_2)_3\underset{H}{CH}{-}\underset{HSO_4}{CH}{-}CH_2CH_2SO_3H \longrightarrow CH_3(CH_2)_3CH_2\underset{O\text{———}}{CH}CH_2CH_2\underset{\text{—}|}{SO_2} + H_2SO_4$$



REACTIONS OF OCTANE-SULTONE

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[8] E. P. Kohler, *Am. Chem. J.*, 20, 680 (1898).

The formation of this octane-sultone in the alcohol plant is still rather obscure; ordinary ethyl alcohol is known to react with fuming sulfuric acid by the well-known carbyl sulfate reaction to yield an hydroxyethylsulfonic acid and a similar reaction might occur here. Another explanation is given in the preceding series of reactions.

Experimental

Extraction and Purification of the Octane-sultone.—The crude material is grayish black and so finely divided as to appear amorphous. It was pulverized in a mortar with repeated additions of cold gasoline until all odor of the original mother liquor was removed as well as any adhering oil, that is, until the last gasoline wash became colorless. The residue was then extracted with boiling 90% benzol and filtered. A fine crop of crystals was produced by adding three volumes of gasoline to the benzol solution. The precipitation under these conditions is practically complete after standing overnight. The excess solvent was drained from the crystals, the latter were redissolved in benzol and again precipitated with three times the volume of gasoline. The gasoline used was normal benzine, a specially treated and steam distilled product which was free from heavy oils and unsaturated compounds. The process was repeated, the resulting crystals were dried for two days at 85°, pulverized and dried again overnight at 85°.

Anal. Calcd. for $C_8H_{16}SO_3$: C, 49.97; H, 8.33; S, 16.75; O, 24.95. Found: C, 49.70; H, 8.64; S, 16.73; O (by difference), 24.93; N, none; ash, none.

The molecular weight was determined by the freezing-point method using benzol as solvent and was found to be 188 as compared with the theoretical molecular weight, 192.

The compound is very stable; it has a very faint camphor-like odor, especially when heated. It melts sharply at 129° and sublimes without decomposition when melted in small quantities. When melted in large quantities, partial decomposition takes place with evolution of sulfur dioxide and a black tarry mass is left behind. It distils very readily with steam and can also be purified by crystallization from hot water, from which it comes out in long prismatic needles belonging to the monoclinic system. It can also be purified by evaporation of the benzol solution.

TABLE II

SOLUBILITY IN VARIOUS SOLVENTS

Solvent	Temp., °C.	Wt. %	Solvent	Temp., °C.	Wt. %
Water	100	1.55	Methyl alcohol	20	13.15
Water	20	0.025	Abs. ethyl alc.	20	4.98
Ethyl ether	20	4.84	Ethyl alc. 95%	20	5.21
Benzene, 90%	20	25.88	Isopropyl alc.	20	4.37
Chloroform	20	55.57	Normal benzine (above)	20	0.22
Acetone	20	52.43			

Specific gravity at 20°, 1.2973.

The yield from the original material as obtained from the refinery was as follows

Adhering oils	62.35%	soluble in benzol
$C_8H_{16}SO_3$	19.45%	
Residue	18.20%	insoluble in benzol
Total	100.00%	

The above insoluble residue, which was of a light gray color, was pulverized, dried at 60° and found to have the following composition

Analysis of residue insoluble in benzol

Ferrous sulfate	82.08%	
Sodium sulfate	1.40%	
Free sulfuric acid	0.26%	
Water of crystallization	13.16%	(by difference)
Silica	0.35%	
Basic ferrous sulfate	2.75%	(water insoluble)
Total	100.00%	

It is thought possible that the presence of such a large quantity of ferrous sulfate might help the formation of the sultone by maintaining reducing conditions in the solution.

Barium Salt Type "A" of Octane-sultone.—Fifty grams of octane-sultone is refluxed for four hours with 30 g. of barium hydroxide in 500 cc. of water in a 2-liter flask to avoid foaming over; the sultone goes completely into solution, the hot liquid is filtered to remove traces of insoluble matter, diluted with twice its volume of water to facilitate precipitation of the barium carbonate and saturated with carbon dioxide. The barium carbonate is filtered off and the liquid is carefully evaporated to dryness on the water-bath. It is purified for analysis by dissolving it in a mixture of absolute alcohol and ether, filtering and blowing air over the solution until crystals appear, when it is left in the ice box for an hour to finish the crystallization. The third or fourth recrystallization gives fine white needles. The salt can be crystallized from water but on drying it decomposes partially and the barium content is high. The silver salt is prepared by double decomposition of the barium salt with silver sulfate suspended in water, and is purified by crystallization from acetone. The potassium salt is prepared from octane-sultone and potassium hydroxide and is purified by dissolving in a mixture of absolute alcohol and benzol, adding gasoline and evaporating by blowing a current of air over the solution.

Anal. Calcd. for $C_{16}H_{32}O_7S_2Ba$: Ba, 25.50. Found: Ba, 25.58, 25.61, 25.57, 25.50. Calcd. for $C_{16}H_{32}O_7S_2Ag_2$: Ag, 34.97. Found: Ag, 35.22. Calcd. for $C_{16}H_{32}O_7S_2K_2$: K, 1633. Found: K, 16.46.

Octane-sultone from Barium Salt Type "A."—Twenty grams of octane-sultone is refluxed for four hours with 10 g. of barium hydroxide and 100 cc. of water, the filtered solution is treated with enough sulfuric acid in the cold to precipitate all of the barium, then with enough concentrated sulfuric acid to make up a 5% solution and refluxed for an hour. The octane-sultone comes out as an oil that solidifies on cooling; yield of crude product, 10 g. The crude material is purified by recrystallization from alcohol and melted at 129°; a mixture of this substance and some of the original octane-sultone melted at 129°, too.

Bromo-octane-sultone Type "A*"—Twenty-five grams of octane-sultone is refluxed with 200 cc. of a 15% solution of potassium hydroxide for twenty hours, or until all of the sultone is dissolved. To the cooled solution bromine is carefully added until the contents turn red, excess bromine is removed by acidifying and adding sodium sulfite, and the whole is cooled in ice until the pasty precipitate has turned brittle so that it can be collected on a Büchner funnel; yield of crude material, 34 g. against 35.3 g. theoretical. The compound is purified by crystallization from alcohol, from which solvent it comes out in fine white needles; m. p. 112°.

Anal. Calcd. for $C_8H_{15}BrSO_3$: C, 35.50; H, 5.57; S, 11.81; Br, 29.44. Found: C, 35.32; H, 5.67; S, 12.40; Br, 29.10.

The chlorine derivative was made in the same way, chlorine gas being bubbled into the solution until a test sample did not decolorize bromine water; m. p. 122.5".

Anal. Calcd. for $C_8H_{15}ClSO_3$: C, 42.46; H, 6.66; S, 14.12; Cl, 15.62. Found: C, 42.86; H, 6.86; S, 13.99; Cl, 15.68.

From 0.1 to 0.3 g. of the purified barium salt of the octane-sultone Type "A" was dissolved in water and titrated with $N/10$ bromine in glacial acetic acid. The end-point is so sharp that a back-titration is not required, the first appearance of a faint yellow color persisting for a few minutes being taken as the end-point. The atoms of bromine required per molecule of $C_{16}H_{32}S_2O_7Ba$ were in one case 3.98 and in another case 3.96. This indicates that the reactiop proceeds thus

$$C_{16}H_{32}S_2O_7Ba + 2\ Br_2 \longrightarrow 2C_8H_{15}BrSO_3 + BaBr_2 + H_2O$$

The same bromine derivative was made from solutions prepared by hydrolyzing octane-sultone with barium hydroxide, with sodium hydroxide or with sodium or potassium carbonate in 20% concentration.

Hydrolysis of the Bromo-octane-sultone Type "A."—Fifty grams of bromo-octane-sultone Type "A" was refluxed with one liter of water, to which was added 1.5 moles of barium hydroxide, for two hours or until the bromine derivative went into solution; the liquid was filtered hot and allowed to cool, when a crop of the barium salt crystallized out and was purified by crystallization from alcohol. The potassium salt was prepared in the same way. They are both anhydrous.

Anal. Calcd. for $C_{10}H_{30}Br_2S_2O_7Ba$: Ba, 19.73. Found: Ba, 19.77, 19.85, 19.72. Calcd. for $C_{16}H_{30}Br_2S_2O_7K_2$: K, 12.27. Found: K, 11.64.

Preparation of Free Bromo-octane-oxysulfonic Acid.—The barium salt of the sulfonic acid was changed into the free acid by dissolving it in water, in which it is quite soluble, adding a slight excess of sulfuric acid to precipitate all the barium, boiling the filtrate with lead carbonate to remove excess sulfuric acid, filtering, precipitating the lead with hydrogen sulfide, refiltering and carefully concentrating on the water-bath to a sirup, which crystallizes in a few days. This solid is then dried by pressing onto porous plates and is purified by crystallizing several times from benzol; m. p. 90°. The presence of slight traces of mineral acids in the solution gives the compound a purple color.

Barium Salt Type "B" of Octane-sultone.—Twenty-five grams of octane sultone was refluxed for twelve to sixteen hours with 14 g. of barium carbonate and 50 cc. of water, the hot liquid is filtered to remove traces of insoluble matter, and cooled. Should any of the barium salt crystallize out it is removed, as the crystallizable salt is Type "C;" the filtrate can be concentrated down to a sirup but will not crystallize out.

Bromo-octane-sultone Type "B."—The sirupy barium salt Type "B" is diluted with water and to the cooled solution bromine is added until the upper layer turns red, excess bromine is removed by acidifying and adding sodium sulfite and the whole is cooled in ice until the pasty precipitate has turned brittle so that it can be collected on a Buchner funnel. A certain amount of a brominated oil will always be formed and run through the Buchner funnel into the receiver; this comes from the barium salt Type "C" which is always present to a certain extent. The precipitate is purified by crystallization from alcohol, from which solvent it comes out in fine white needles; m. p. 139°. The chlorine derivative is made in the same way; m. p. 118.5°.

Anal. Calcd. for $C_8H_{15}BrSO_3$: C, 35.50; H, 5.57; S, 11.81; Br, 29.44. Found: C, 35.65; H, 5.80; S, 12.30; Br, 29.49; 29.32, 30.00.

Anal. Calcd. for $C_8H_{15}ClSO_3$: C, 42.46; H, 6.66. Found: C, 42.79; H, 6.90.

Hydrolysis of Chloro-octane-sultone Type "B" and Subsequent Closing of Sultone Ring to Form Octene-sultone.—Ten grams of octane chloro-sultone Type "B" is refluxed with 15 g. of barium hydroxide in 80 cc. of water for an hour, the solution is cooled, a slight excess of sulfuric acid is added and the barium sulfate filtered off. Ten cc. of concentrated sulfuric acid is then added to the filtrate, which should amount to about 200 cc., and the acid solution is refluxed for an hour to close the sultone ring. The sultone comes out as an oil which solidifies on cooling; it is collected on a Buchner funnel and dried at 60°; yield, 7.3 g. of crude substance or 86% of the theoretical. The crude is purified by repeated crystallization from dilute alcohol, from which it comes out in beautiful white needles over an inch long; m. p. 92.5".

Anal. Calcd. for $C_8H_{14}SO_3$: C, 50.59; H, 7.40; S, 16.79. Found: C, 50.67; H, 7.59; S, 17.26.

The barium salt of this unsaturated sultone is a sirup; hydrolysis of the chlorosultone lactone Type "B" in acid solution causes decomposition.

Preparation of Bromo-octene-suitone.—About ten to twenty grams of the sodium salt of octene sultone in aqueous alkaline solution is treated with bromine until a permanent yellow color is obtained. The precipitate is crystallized from alcohol; m. p. 117°.

Anal. Calcd. for $C_8H_{13}BrSO_3$: C, 35.77; H, 4.87; S, 11.97; Br, 29.66. Found: C, 35.93; H, 5.13; S, 12.55; Br, 29.96.

Calcium Salt Type "C" of Octane-sultone.—Twenty-five grams of octane-sultone is refluxed with nine grams of calcium carbonate and 400 cc. of water overnight, the solution is filtered hot and concentrated. The calcium salt comes out in white pearly plates; yield, first crop, 9.8 *g.*; second crop, 9 g.; third crop, 7.5 g.

The barium salt was made in the same manner, using a larger excess of barium carbonate; the yield is not as good.

Anal. Calcd. for $C_{16}H_{32}O_7S_2Ba$: Ba, 25.50. Found: Ba, 25.21, 25.35.

Octyl Bromides.—On treating the above salts in alkaline solution with bromine a heavy oil is deposited that on distillation under vacuum gives a lighter fraction lighter than water and a heavier fraction heavier than water. Purification was not successful.

Octene.—Two hundred and fifty grams of the calcium salt of octane-sultone Type "C" was dissolved in 1000 cc. of water, a slight excess of sulfuric acid added to precipitate all the calcium and the mixture was steam distilled. An octene came over and was carefully fractionated twice; yield of crude olefin, 130 g. (61%). 96% of this olefin distils between 113 and 115°, the remainder between 110 and 113°. Repeated distillation does not effect a further separation. The olefin does not give a solid nitrosochloride.

Anal. Bromine absorbed: 171, 169 g. per 112 g. of olefin, as against 160 g. required for C_8H_{16}.

Acknowledgment.—The writers wish to express their appreciation and thanks to M. G. Gardella for his carbon and hydrogen determinations and to C. C. Callis for the molecular weight determination.

Summary

1. A compound of empirical formula $C_8H_{16}SO_3$ has been obtained from one of the by-products of the manufacture of alcohols at the Bayway Re-

finery of the Standard Oil Co. (N. J.) and separated as crystals of a high degree of purity.

2. The compound is undoubtedly an octane-sultone, since its behavior is strictly analogous to that of sultones in the aromatic and camphene series.

3. On refluxing with alkalies various alkaline salts are obtained whose different chemical properties are explained by a shifting of the double bond generated from the hydroxyl group.

4. Attempts are now being made to synthesize sultones in the aliphatic series.

5. The compound is interesting to the petroleum technologist as it is volatile in steam; hence aliphatic sultones may be partly responsible for the sulfur content of refined gasolines.

P. O. BOX 276, ELIZABETH, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH]

REACTIONS OF VINYL CHLORIDE AND BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

BY JAMES M. DAVIDSON WITH ALEXANDER LOWY

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The purpose of this investigation has been to study the reactions of vinyl chloride and benzene in the presence of aluminum chloride, under variable conditions, in order to determine the course of the reactions and to study the products formed. These reactions seemed important since vinyl chloride has recently been prepared in large quantities.

Boeseken and Bastet[1] found that vinyl chloride and benzene condensed in the presence of a catalyst made from aluminum and mercuric chloride, and produced chiefly unsymmetrical diphenylethane and a small quantity of 9,10-dimethyldihydro-anthracene. Vinyl bromide and benzene were found to react in the presence of aluminum chloride by Angelbis and Anschütz,[2] and Anschütz,[3] and yielded the identical products described by Boeseken and Bastet. Hanriot and Guilbert[4] obtained products believed to have been β-bromo-ethylbenzene and *p*-di-(β-bromo-ethyl)-benzene in the same reaction.

From the nature of the Friedel–Crafts reaction, styrene would be expected as an intermediate in the reaction under consideration. Schramm[6] obtained unsymmetrical diphenylethane from the reaction between styrene, benzene and aluminum chloride, but Boeseken and

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[1] J. Boeseken and M. C. Bastet, *Rec. trav. chim.*, 32, 184 (1913).

[2] A. Angelbis and R. Anschütz, Ber., 17, 165, 167 (1884).

[3] R. Anschutz, Ann., 235, 159,299 (1886).

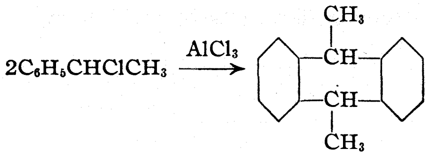
[4] Hanriot and Guilbert, *Compt. rend.*, 98, 525 (1884).

[5] *J. Schramm, Ber.,* 26,1709 (1893).

Bastet described polymerization of styrene under these conditions. The present investigation showed that styrene did polymerize in the presence of benzene and aluminum chloride, and could not have been an intermediate in the reaction between vinyl chloride, benzene and aluminum chloride. Unsymmetrical diphenylethane and an anthracene-type resin were the main products isolated and under special conditions 9,10-dimethyldihydro-anthracene was also obtained. In previous work no mention has been made of this resin.

The following schematic outline substantiated the reactions given by Boeseken and Bastet, in which they used the Al–$HgCl_2$ catalyst

$$C_6H_6 + CH_2 = CHCl \xrightarrow{AlCl_3} C_6H_5CHClCH_3 \xrightarrow[C_6H_6]{AlCl_3} (C_6H_5)_2CHCH_3$$



The reactions, as carried out at 0–5°, tended to produce only traces of 9,10-dimethyldihydro-anthracene and relatively large amounts of unsymmetrical diphenylethane and resinous substances. Both of the latter substances were found to decrease if the temperature was maintained at 60–70°, and appreciable amounts of 9,10-dimethyldihydro-anthracene were formed. Similar results were obtained when 0.1 g. of iodine, originally used to prevent the polymerization of styrene, was present.

Experimental

Considerable preliminary experimental work was done to study the rate of addition of vinyl chloride, the temperature effects, and the variation of addition of components to the reaction mixture.

Description of a Typical Experiment.—Fifty grams of anhydrous aluminum chloride and 300 cc. of benzene (thiophene free, dried over sodium) were agitated in a one-liter three-necked flask, provided with an upright condenser, thermometer, gas inlet tube and a stirrer run at 1000–1400 r.p.m., until the aluminum chloride was in a finely divided state. Vinyl chloride gas, supplied in small cylinders by the Carbide and Carbon Chemicals Corporation, was passed into the flask, kept at 0–5°, at such a rate that only a few bubbles of gas escaped from an alkali trap connected to the condenser. No evolution of hydrogen chloride was observed until after an initial period of fifteen to twenty minutes. After 90 g. of gas had been added, all of the hydrogen chloride apparently had been evolved.

The reaction mixture was poured into ice, acidified with hydrochloric acid and, after the heavy black layer had completely disappeared, the fluorescent brown top layer was separated, washed with water and steam distilled. The distillate, consisting chiefly of unreacted benzene, was dried and fractionated. Besides benzene, some ethylbenzene was obtained in the fraction boiling at 130–135°. In no case was a styrene fraction (140–145°) obtained.

The residue from the steam distillation was a very viscous, fluorescent, greenish oil. This was distilled under reduced pressure in a 500-cc. Claisen flask. Water was removed first at 50-mm. pressure, after which unsymmetrical diphenylethane distilled at 130–140° under 12-mm. pressure. The latter was a nearly colorless oil, but possessed a strong violet fluorescence. On redistillation most of the fraction boiled at 134–136° (12 mm.). Above 140° the pressure was reduced to 0.5 mm., and traces of 9,10-dimethyldihydro-anthracene sublimed from 180–200". The residue was poured into a beaker and solidified on cooling to a dark green resin having a reddish fluorescence when in solution.

Occasionally the residue from the steam distillation crystallized on standing. In this event the solid was filtered and crystallized from alcohol. It was identified as 9,10-dimethyldihydro-anthracene, and possessed the following characteristics: yellow platelets, melting at 179–181°, purplish fluorescence in solution. The oily filtrate was distilled as described above.

The following table outlines the purpose, details and results obtained in experiments performed under variable conditions.

TABLE OF RESULTS

Purpose of expt.	Reagents		Temp., °C.	Time, hrs.	Products			
	$AlCl_3$, g.	Vinyl chloride, g.			A, g.	B, g.	C, g.	D, cc.
Variation of reagents	2	90	0–5	2	4	10	tr.	50
	50	90	0–5	2	3	46	tr.	40
	133.5 (1 mole)	90	0–5	2	4	35	tr.	60
	267 (2 moles)	90	0–5	2	7	32	tr.	15
	133.5	60	0–5	1.5	6	23	tr.	20
Effect of heat	50	90	0–5	1.5				
			then 60–70	2	4	32	tr.	60
	50	90	60–70	2	4	13	17	33
Addn. of 0.1 g. of iodine	133.5	90	*0–5*	1.5	4	10	20	25
Addn. of 1 g. of Hg	50	90	0–5	1.5	..	..	..	..
			then 60–70	2	15	17	tr.	20

[a] A, Ethylbenzene; B, unsymmetrical diphenylethane; C, 9,10-dimethyldihydro-anthracene; D, resin. 300 cc. of benzene was used in each of the above experiments.

Discussion of Results

A maximum quantity of unsymmetrical diphenylethane was obtained with 50 g. of aluminum chloride. Very small amounts of aluminum chloride gave smaller yields of all the products, while larger amounts of this reagent tended to diminish the yield of unsymmetrical diphenylethane. Holding the aluminum chloride constant and diminishing the amount of vinyl chloride added reduced the quantities of products formed, as expected. Larger amounts of vinyl chloride could not be absorbed by the reaction mixture.

When the reacting compounds were heated from the start, a relatively large amount of 9,10-dimethyldihydro-anthracene was obtained. This could not have been a product at the lower temperature, since heating of the cold reaction product did not cause the formation of this compound.

The amounts of resin and unsymmetrical diphenylethane were decreased in the first instance, but the amount of resin increased at the expense of the unsymmetrical diphenylethane after the reaction products formed in the cold had been heated. This seemed to indicate that the resin was formed by the action of aluminum chloride upon unsymmetrical diphenylethane.

The presence of a trace of iodine was sufficient to accelerate the reaction, for hydrogen chloride was evolved immediately, At the same time there was a relatively large amount of 9,10-dimethyldihydro-anthracene formed and the amounts of resin and unsymmetrical diphenylethane were reduced.

Mercury caused the reduction of α-phenylchloro-ethane, probably formed as an intermediate, to ethylbenzene. The amounts of resin and unsymmetrical diphenylethane were also reduced. The reducing power of mercury accounted for the formation of large quantities of ethylbenzene and polyethylated benzenes obtained during a preliminary experiment, when a mercury-seal stirrer was used.

Effect of Carbon Disulfide.—Carbon disulfide was used as a solvent or diluent in one experiment. Sulfur-containing oils, formed probably by the condensation of vinyl chloride and carbon disulfide, were obtained, but they were not related to the products of the normal reaction.

Study of the Resin.—The resin, which was a brittle, dark green solid possessing a reddish fluorescence in solution, melted at 50–65°. It was soluble in benzene, acetone and glacial acetic acid, slightly soluble in alcohol, but insoluble in water, acids or alkalies. It contained no halogen and therefore was not a vinyl chloride-type resin.

On heating the resin formed a dark green, fluorescent liquid which was very viscous. Although heated to 300°, no *traces* of 9,10-dimethyldihydro-anthracene were observed. Instead of sublimation, there was a noticeable decomposition. When heated to 220° under 0.5-mm. pressure, small amounts of 9,10-dimethyldihydro-anthracene were obtained. Continued heating caused decomposition.

A benzene solution of styrene, when treated with aluminum chloride under the normal experimental conditions, yielded a resin different from those obtained with vinyl chloride, since styrene was obtained by heating it.

Oxidation of a solution of the resin in glacial acetic acid and benzene with chromium trioxide produced anthraquinone, indicating an anthracene-type resin. No crystalline picrate could be obtained from the resin and the exact identity of the hydrocarbon constituent of the resin could not be learned.

Summary

1. The reaction of vinyl chloride and benzene in the presence of aluminum chloride took place with the formation of unsymmetrical diphenylethane, 9,10-dimethyldihydro-anthracene and an anthracene-type resin. No styrene or metastyrene was formed. a-Phenylchloro-ethane has been considered as the most probable intermediate.

2. Increased amounts of aluminum chloride at low temperatures decreased the amounts of unsymmetrical diphenylethane.

3. The amounts of 9,10-dimethyldihydro-anthracene were increased by using a higher temperature, or by the presence of iodine.

4. Mercury caused the formation of ethylbenzene and considerably reduced the amount of resin formed.

5. Certain physical and chemical properties of the resin have been studied.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. JOHN'S COLLEGE]

THE BECKMANN REARRANGEMENT IN THE PRESENCE OF FREE RADICALS

BY EVERETT S. WALLIS[1]

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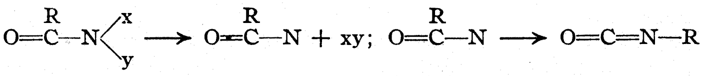
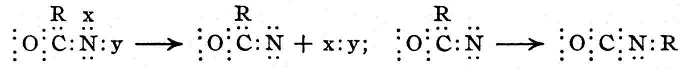
Of the several theories that have been advanced to explain the rearrangement of hydroxamic acids, halogen amides, acyl azides and other similar classes of compounds, the most successful has been the interpretation by Stieglitz.[2] Assuming the intermediate formation of a univalent nitrogen derivative, he proposed that all rearrangements of this character take place as follows



$$O{=}\overset{R}{C}{-}N\left\langle\begin{matrix}x\\y\end{matrix}\right. \longrightarrow O{=}\overset{R}{C}{-}N + xy;\quad O{=}\overset{R}{C}{-}N \longrightarrow O{=}C{=}N{-}R$$

Jones and Hurd,[3] suggesting an interpretation of the mechanism of these rearrangements based upon the modern conception of chemical bonds and electrons, formulated the rearrangement thus



$$\vdots O \vdots \overset{R}{C} : \overset{x}{\ddot{N}} : y \longrightarrow \vdots O \vdots \overset{R}{C} : \ddot{N} + x : y;\quad \vdots O \vdots \overset{R}{C} : \ddot{N} \longrightarrow \vdots O \vdots C \vdots \ddot{N} : R$$

Their interpretation, which excluded the oximes, assumed that the radical, R, in its wandering from the carbon atom to the nitrogen atom existed momentarily as a free radical, and that the relative ease of rearrangement of such types of compounds depended upon the tendency of the radical, R, in the univalent nitrogen derivative to exist as a free radical. This hypothesis was tested by studying the rearrangement of monophenyl-, diphenyl- and triphenylacethydroxamic acids and their derivatives.

Hurd[4] also found further evidence in support of this hypothesis in his study of certain derivatives of N-diphenylhydroxyurea, $(C_6H_5)_2N$-CO-NHOH.

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[1] Some of the preliminary experiments in this investigation, including the preparation of materials, etc., were carried out with the help of Mr. Howard W. Gilbert, a graduate assistant in the department.

[2] Stieglitz, Am. *Chem.* J., 18, 751 (1896); *ibid.*, 29, 49 (1903); Stieglitz and Earle, *ibid.*, 30,349,412 (1903); Stieglitz and Slossen, *Ber.*, 28, 3265 (1895); 34, 1613 (1901); Stieglitz and Leech, THIS JOURNAL, 36, 272 (1914).

[3] Jones and Hurd, *ibid.*, 43, 2422 (1921).

[4] Hurd, *ibid.*, 45, 1472 (1923).

Continuing these investigations Jones and Wallis[5] studied the nature of the products formed by the rearrangement of certain acid azides and hydroxamic acids in which the group, R, is an optically active radical. d-Benzylmethylacetazide, $C_7H_7(CH_3)HCCON_3$, was found to give on rearrangement an optically active isocyanate, $C_7H_7(CH_3)HCNCO$, which could be converted into an optically active amine hydrochloride, and by treatment with aniline into an optically active monosubstituted urea. These experiments, together with certain other facts taken from a survey of the properties of optically active compounds described in the literature, led them to suggest that it was very probable that in the rearrangement of d-benzylmethylacetazide the optically active radical, R, if existing as a free radical, did so in such *a* way as to maintain a configuration required to produce an optically active rearrangement product; that is, it was, as originally supposed by Jones,[6] a positive radical which is of the nature of a carbonium ion, and that in its wandering from the carbon atom to the nitrogen atom it leaves behind the electron which it shared with the carbon atom.

The Rearrangement of Benzylmethylacetazide in the Presence of a Free Radical.—I have continued these investigations in order to determine the products formed by rearrangement when the rearrangement is carried out in the presence of a free radical; for I believed that such a determination would give further evidence in support of the hypothesis just outlined.

It has been known for some time that triphenylmethyl, because of its preeminent tendency to make addition compounds, is a good reagent for the detection of free radicals. Wieland,[7] for instance, used it in his study of tetraphenylhydrazine, and the assumption that the dehydrophenols[8] contain monovalent oxygen, and that the tetrazanes[9] are dissociable to form triarylhydrazils is based upon the fact that both classes of compounds readily combine with triphenylmethyl. It therefore seemed possible that this same interesting and very reactive compound might be used to advantage in a further study of those classes of compounds that undergo the Beckmann rearrangement. For this investigation benzylmethylacetazide was chosen as a compound typical of this group of substances. It was allowed to rearrange in the absence of air in a benzene solution of triphenylmethyl and the products of the rearrangement were determined. With no triphenylmethyl present the rearrangement has been formulated[6] as follows

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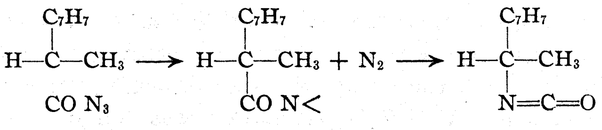
[5] Jones and Wallis, This Journal, 48, 169 (1926).

[6] Jones, *Am. Chem.* J., 50, 441 (1913).

[7] H. Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart.

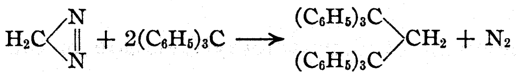
[8] S. Goldschmidt, *Ber.* 53, 44 (1920); *ibid.*, 55, 616, 628 (1922).

[9] S. Goldschmidt, *ibid.*, 55, 3194, 3197 (1922).



$$\underset{\text{CO N}_3}{\overset{C_7H_7}{\text{H—C—CH}_3}} \longrightarrow \underset{\text{CO N}<}{\overset{C_7H_7}{\text{H—C—CH}_3}} + N_2 \longrightarrow \underset{\text{N=C=O}}{\overset{C_7H_7}{\text{H—C—CH}_3}}$$

However, a little reflection will show that when triphenylmethyl is present two different rearrangement products are possible. (1) If the radical, R, in the univalent nitrogen derivative, in its wandering from the carbon atom to the nitrogen atom exists momentarily as a true free radical, that is, does not leave behind on the carbon atom its electron and so become a positive ion, the formation of two different isocyanates is possible. The radical triphenylmethyl, can then compete with the radical, R, for the univalent nitrogen residue, and the quantity of triphenylmethyl isocyanate, $(C_6H_5)_3CNCO$, so formed would depend on well-known physical-chemical principles. An illustration of such a phenomenon is found in the reaction of diazomethane and triphenylmethyl. Investigations[10] have shown that these two substances react according to the equation



Here, apparently, the free radical, triphenylmethyl, when in the proper concentration, is so successful in its competition with the methylene radical for union with another methylene radical that no ethylene seems to be formed in the reaction.

(2) However, if the radical, R, in its wandering from the carbon atom to the nitrogen atom, leaves behind its electron and becomes a positive ion as suggested by Jones and Wallis,[5] the chances of the formation of any triphenylmethyl isocyanate would be very slight. In fact the radical, R, would then be of an entirely different nature than the free radical, triphenylmethyl, and only the one isocyanate, $C_7H_7(CH_3)HCNCO$, would be expected.

The author's experiments on the rearrangement of benzylmethylacetazide in the presence of triphenylmethyl seem to give further evidence which tends to exclude the first possibility, and to show that the latter view of the rearrangement is the more probable. When a benzene solution of benzylmethylacetazide was added to a benzene solution of triphenylmethyl, and the rearrangement allowed to take place in the absence of air, a quantitative determination of the amount of oxygen absorbed by the free radical remaining after the rearrangement indicates that none of it took part in the reaction, and an analysis of the products of the rearrangement shows that only one isocyanate, $C_7H_7(CH_3)HC\text{-}NCO$, is formed in appreciable amounts.

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[10] Schmidlin, "Triphenylmethyl," Ferdinand Enke, Stuttgart (investigator, Schlenk).

Experimental Part

Materials.—The benzylmethylacetazide used in these investigations was prepared by the action of sodium azide on benzylmethylacetyl chloride dissolved in ether according to a method previously described.[5] The purity of the azide was determined by measuring quantitatively the amount of nitrogen evolved when the compound undergoes rearrangement. The solid triphenylmethyl used in these experiments was prepared and its purity determined according to the method of Gomberg.[11] The benzene used was of the purified variety that is commonly employed in investigations involving the use of free radicals.

Procedure.—A three-holed round-bottomed flask immersed in a thermostat was connected by means of glass tubing containing stopcocks to three azotometers[12] filled with benzene. After the air had been completely removed from the apparatus a known volume of benzene was run into the flask by means of a dropping funnel and a weighed portion of solid triphenylmethyl was introduced. When solution had taken place a weighed amount of benzylmethylacetazide dissolved in a small amount of benzene was added. The stopcocks in the azotometers were opened and the rearrangement was allowed to take place at a constant temperature. The volume of nitrogen evolved was measured and corrected to standard conditions of temperature and pressure. After the rearrangement was completed all stopcocks were closed and the azotometers were disconnected and filled with dry oxygen. After being again connected to the reaction flask, the stopcocks were opened and the oxygen was allowed to diffuse into the reaction chamber and be absorbed by the triphenylmethyl remaining in the solution. The flask was shaken vigorously from time to time and the volume of oxygen absorbed was measured and corrected to standard conditions of temperature and pressure. Several experiments were carried out varying the temperature at which the rearrangements took place and the concentrations of the benzylmethylacetazide and triphenylmethyl. In all cases the volume of oxygen absorbed after the rearrangement corresponded very closely to the theoretical amount of absorption expected if no triphenylmethyl had taken part in the reaction. The results are given in Table I.

TABLE I[a]

TABULATED RESULTS

Expt.	Rearrangement temp., °C.	Azide, g.	Triphenylmethyl g.	Soln., cc.	N_2 corr. to S.T.P., cc.	N_2, calcd., cc.	O_2 abs. corr. to S.T.P. cc.	Calcd. vol. of O_2 abs. assuming no triphenylmethyl reacted, cc.
1	35	1.023	...	60	118.3	121.2	...	...
2	35	...	1.192	60	...	...	53.9	55.0
3	35	0.887	1.203	60	103.0	105.2	56.1	55.5
4	50	1.097	1.314	60	127.2	130.1	59.2	60.6
5	35	1.147	2.864	60	133.3	137.0	129.8	132.1

[a] The vapor pressures of benzene used in these calculations were taken from tables published in Landolt and Bornstein. In Expt. 5 about two moles of triphenylmethyl were used for 1 mole of azide.

Analysis of the Products of Rearrangement.—An analysis was carried out of the products of rearrangement in Expt. 5. The benzene was partially removed by evaporation at room temperature in a vacuum desiccator. The triphenylmethyl peroxide,

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[11] Gomberg and Cone, *Ber.*, 37, 2034, **3638 (1904).**

[12] Three azotometers were necessary since in some of the experiments the amount of azide used gave more than 100 cc. of nitrogen on rearrangement.

formed by the action of the oxygen on the triphenylmethyl, was collected on a filter and washed with a small amount of benzene: 2.38 g. of dry product was obtained, melting point, 183'. One recrystallization from carbon disulfide gave a product melting at 185°. The recorded melting point of pure triphenylmethyl peroxide is 185–186°; yield of peroxide, 78%. The filtrate was analyzed for any isocyanates that might be present. Dry ammonia gas was passed through the solution and in a few minutes a white precipitate of the urea was obtained. This was collected on a filter, after 25 cc. of ligroin had been added to decrease its solubility in the benzene solution; 1.00 g. of dry product was obtained, melting point 146°. One recrystallization from alcohol and water gave a solid melting at 149'; yield assuming but the one isocyanate to have been formed, 97%.

The filtrate from the urea was concentrated and some oily products were obtained. Attempts to isolate any compounds of known constitution that might be expected to be formed failed. In all probability these oily products are produced by the decomposition of the triphenylmethyl peroxide. As has been already stated in the literature, although the absorption of oxygen by triphenylmethyl is nearly quantitative, the amount of triphenylmethyl peroxide obtained from a known weight of triphenylmethyl is not quantitative; other substances of unknown constitution are produced.

Summary

The Beckmann rearrangement of an acylazide in the presence of a free radical has been studied, and the products of the rearrangement have been determined. Benzylmethylacetazide was allowed to rearrange in the absence of air in a benzene solution of triphenylmethyl. Evidence is submitted in this paper to show that only one isocyanate, benzylmethylisocyanate, is formed. A discussion of this fact with reference to certain theories on the Beckmann rearrangement is given.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE COLLEGE]

A CLEAVAGE OF AZO DYES BY MEANS OF SULFITES*

BY KARL H. ENGEL

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Cleavage of azo dyes through the action of sulfurous acid or of acid sulfites has frequently been observed heretofore but, apparently, has not been investigated in detail. A few experiments of the writer, the interaction of 4-hydroxyazobenzene and sodium bisulfite, for example, indicated that a cleavage of the dye was apt to be complicated by various secondary changes, the rearrangement of primary reaction products sometimes, the formation of resinous by-products and a reduction of some of the azo nitrogen to ammonia. In short, such a reaction looked rather unpromising.

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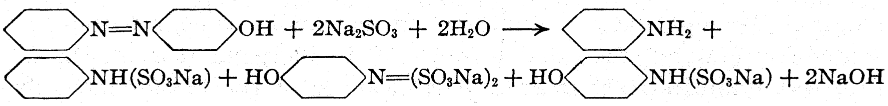
* The material here presented has been submitted as a thesis in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Pennsylvania State College.

A number of years ago, however, the author made the observation that neutral alkali or ammonium sulfites react with azo dyes, in an exact ratio of two moles of sulfite to one mole of dye, resulting in a clear-cut fission of the dye between the two nitrogen atoms of the azo group. The reaction does not parallel the reduction by means of hydrosulfite, which, as is well known, leads to the formation of two primary amines. The sulfite cleavage, it is true, also yields a certain amount of primary amine. It differs in that the reacting sulfite tends to combine with the nitrogen atom attached to the secondary dye component, to a smaller extent with the nitrogen of the primary component. 4-Hydroxyazobenzene, for example, yields the following primary cleavage products



The formation of N-sulfonic acids points to certain similarities with the sulfite reduction of aromatic nitro and nitroso compounds. As expected, the resulting N-sulfonic acids, according to their specific nature, may either hydrolyze or rearrange, in the presence of mineral acids.

Some forty monoazo dyes were treated with ammonium, sodium or potassium sulfite, the dyes comprising hydroxy- and amino-azobenzene derivatives as well as dyes which contained hydroxy- or aminonaphthalene derivatives as secondary components. Most of these were found to react according to the scheme above. In a few cases, 2,4-dihydroxyazobenzene, for example, only two cleavage products were obtained: the original primary amine (aniline) and the N-disulfonic acid of the secondary component, of aminoresorcinol. A totally unsulfonated nitrogen of the secondary component was not observed, except in one instance: dimethylaminoazobenzene yielded a trace of dimethyldiaminobenzene.

A detailed investigation of the cleavage of 4-hydroxyazobenzenb and of 4'-hydroxyazobenzene-4-sulfonic acid is the subject of the following pages.

Earlier References.—An interesting cleavage of an azo compound was observed by Schmitt and Bennewitz,[1] who found that aqueous suspensions of 2,2'-dichloro-azobenzene reacted readily with sulfurous acid or sodium bisulfite, yielding a difficultly soluble 1-amino-4-phenol-6-sulfonic acid. A. Spiegel,[2] on heating azobenzene in an alcoholic solution of ammonium bisulfite, obtained a white crystalline reaction product which corresponded to the composition $C_{12}H_{11}N_2SO_3H$. It yielded benzidine sulfate in dilute mineral acid, and was therefore taken to be a monosulfaminic acid of benzidine, $H_2NC_6H_4C_6H_4NHSO_3H$. Bucherer and Sonnenberg[3] heated azobenzene in an aqueous solution of ammonium

[1] Schmitt and Bennewitz, *J. prakt. Chem.*, [2] 8, 7 (1874).

[2] A. Spiegel, *Ber.*, 18, 148 (1885).

[3] H. Th. Bucherer and Sonnenberg, *J. prakt. Chem.*, 81, 33 (1910).

sulfite at 110° and obtained a nearly quantitative yield of the ammonium salt of an N-sulfonic acid of hydrazobenzene, which, like Spiegel's reduction product, yielded benzidine sulfate on addition of mineral acid.

The Cleavage Reaction.—The experimental procedure, briefly, consisted of heating accurately weighed samples of pure dye and measured volumes of sulfite solution in closed containers, generally at 90 to 95°, until the dye was dissolved and decolorized. Primary amines such as aniline could then be separated by extraction or distillation. The N-sulfonic acids, on account of their extreme solubility and their sensitive character, could not be isolated. They rearranged with great ease, as free acids, forming primary amines or sulfonic acids of primary aromatic amines. To supplement the information that might be gained from such secondary products, the reaction course of the inorganic reagent, the sulfite, was quantitatively traced. The cleavage of the unsulfonated dye may be considered representative.

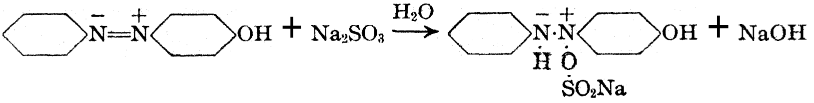
It was found that one mole of 4-hydroxyazobenzene yielded 0.78 mole of free aniline and 0.22 mole of an N-sulfonic acid of aniline, whereas the secondary dye component yielded 0.78 mole of N-disulfonic acid of 1-amino-4-phenol and 0.22 mole of N-monosulfonic acid of 1-amino-4-phenol. On addition of mineral acid to the cleavage products, the N-sulfonic acid of aniline hydrolyzed to give aniline. All of the primary dye component could therefore be recovered in its original form. The secondary dye component, upon rearrangement, yielded 0.54 mole of the insoluble 1-amino-4-phenol-5-sulfonic acid, and 0.46 mole of 1-amino-4-phenol-sulfonic ester, $H_2NC_6H_4OSO_3H$, a compound surprisingly resistant to hydrolytic action of mineral acids and so extremely soluble that it could not be isolated as such, in pure form. In all, two moles of diazotizable amines were ultimately obtained, through cleavage and rearrangements, from one mole of azo dye.

It appeared most likely that a cleavage of an azo group should proceed in two distinct steps, *i. e.*, that formation of N-sulfonic acids of hydrazo bodies should precede a final cleavage. Such intermediate stages, however, have not been observed, so far.

The most interesting feature of the reaction, from a theoretical viewpoint, appeared to be the distribution of the two sulfite molecules between two nitrogen atoms of the azo group. It was observed, in every dye examined, that the two sulfite molecules showed a pronounced tendency to combine with the nitrogen atom attached to the secondary dye component. The nitrogen of the primary component tended to combine with hydrogen. A conclusion that the two nitrogen atoms were marked by rather definitely fixed functional differences suggested itself. Plainly the nitrogen of the secondary component must have functioned very much like the nitrogen of a nitro or nitroso group toward the sulfite, as a positive atom; the nitrogen of the primary dye component, presumably, as a negative atom.[4]

Observation of a number of N-sulfonic acids showed differences, frequently very pronounced, in the character of N-mono- and N-disulfonic acid derivatives of the same amine, particularly in regard to orientation of sulfonic acid groups during rearrangement. Observations of this kind suggested that deeper-lying constitutional differences existed between the N-mono- and N-disulfonic acids in question and it was concluded that only the former were amine derivatives, or "sulfaminic" acids, of a type formula $RNHSO_3Na$; that the N-disulfonic acids, on the other hand, were derivatives of a positive nitrogen, presumably conforming to the type $RN(OSO_2Na)_2$. These various considerations led to the following view regarding the mechanism of the cleavage reaction.

It appeared most likely that an addition product of sulfite molecule and azo group should first be formed, the negative nitrogen joining a sodium atom (or its equivalent hydrogen), the positive nitrogen joining an oxygen of the sulfite molecule and that a reshifting of valency forces should result in a hydrazo derivative



If such a compound suffered no further intramolecular rearrangement, the second sulfite molecule might add and combine in the same manner *as* the first, forming the final cleavage products, aniline and the N-disulfonic acid, $HOC_6H_4N(OSO_2Na)_2$. Yield figures indicated that 78% of the dye could have reacted in this way. The remaining 22% formed N-monosulfonic acids of aniline and of aminophenol. Possibly such products might have been formed following an intramolecular shift of the hydrazo-N-sulfonic acid. The N-disulfonic acid of the experiment might be considered as a sulfurous ester of an hypothetical ortho-nitrous acid derivative, $HOC_6H_4N(OH)_2$. The N-monosulfonic acids, presumably, were true sulfaminic acids, $C_6H_5NHSO_3Na$ and $HOC_6H_4NHSO_3Na$.

The tentatively suggested explanation of the cleavage reaction will be substantiated, it is believed, by further experiments in this field. The reaction may have a practical value as a convenient tool in the synthesis of dye intermediates.

Experimental

Preparation of Materials.—The dyes required were prepared by coupling diazobenzene, or 1-diazobenzene-4-sulfonic acid, respectively, with pure phenol in solutions

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[4] It might be of interest in this connection to recount the origin of the two atoms, the negative one being derived from an aromatic amine, *i. e.*, a substituted ammonia· the positive one from nitrous acid.

containing sodium acetate and acetic acid.[5] 4-Hydroxyazobenzene was repeatedly recrystallized from ethyl alcohol. The pure dye melted at 156.5°, corr.

Anal. Calcd. for $C_{12}H_{10}ON_2$: N, 14.14. Found: N, 14.06.

The sodium salt of the sulfonated dye was recrystallized from water until free from the chlorides originally present.

Anal. Calcd. for $C_{12}H_9O_4N_2SNa$: N, 9.32; S, 10.67; Na, 7.67. Pound: N, 9.29; S, 10.62; Na, 7.63.

A stock solution of ammonium sulfite, approximately 5 N, was prepared from pure ammonia solution and liquid sulfur dioxide. The solution was guarded against air oxidation by keeping the storage bottle filled to capacity with benzene. Slight traces of sulfate were determined and properly discounted later on.

Cleavage of **4-Hydroxyazobenzene.**—19.8200 g. of dye (1/10 mole), and 320 cc. of ammonium sulfite solution, equivalent to 490.3 cc. of a normal solution of sulfurous acid and to 496.7 cc. of a normal solution of ammonia, were placed in nitrogen-filled pressure bottles (to prevent oxidation and loss of volatile substances). Experiments were made in triplicate. The bottles, tightly closed in a reclining position, were heated in a constant-temperature oven at 90 to 93°. The suspended dye, slightly soluble, gradually disappeared. After seventy-two hours, the solution assumed a pale yellowish coloration which did not change on further heating. After seventy-eight hours of continuous heating, the bottle contents were diluted to 500 cc., accurately. Portions of these solutions were used in subsequent analytical determinations.

Removal **of Aniline.**—Aniline formed during cleavage was quantitatively removed from solution by six extractions with 50-cc. portions of benzene. It required 78.8, 78.2 and 77.4 cc. of 1 *N* nitrite solution for diazotization, corresponding to an average yield of 0.78 mole per mole of dye. No trace of 1-amino-4-phenol could be detected in the benzene extract, nor upon complete evaporation of the original solution and extraction of the residue with organic solvents.

After removal of the aniline, a small part of the primary and all of the secondary component of the dye remained in solution. It showed a pronounced bluish fluorescence. A few drops diluted to about 10 cc. showed a beautiful sky blue coloration with ferric chloride in the presence of a little acetic acid. The coloration changed to claret after about thirty minutes.

Attempts were made to isolate the N-sulfonic acids as barium salts. Crystallization, however, did not begin until the solution had been evaporated to a very small volume. The addition of alcohol to more dilute solutions caused a precipitate that was not of uniform composition. These products, dry or in solution, were extraordinarily sensitive to air oxidation, in the absence of protecting traces of sulfite, short exposure causing immediate darkening and an overpowering odor suggestive of isocyanides.

Ammonia, determined in 25-cc. portions, corresponded to 496.4 cc. of 1 N solution, against 496.7 cc. present before cleavage. No ammonia, therefore, could have been generated through reduction of the azo nitrogen.

Aromatic **Amines.**—One hundred-cc. portions, freed from sulfite by addition of barium chloride, required, after addition of concd. hydrochloric acid, 24.2 and 24.4 cc. of 1 *N* nitrite solution for diazotization, potassium iodide–starch indicator giving sharp end-points. One tenth mole of dye, therefore, yielded amines corresponding to 121.5 cc. of 1 N nitrite solution, or 0.121 mole, in addition to the previously isolated 0.078 mole of aniline; one mole of dye yielded a total of 1.99 mole of diazotizable amines

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[5] The reaction was slower under these conditions but yielded cleaner products than the customary coupling in the presence of alkali.

through cleavage and upon addition of acid, cleavage of the azo group had been complete and quantitative. The diazotized solution contained diazobenzene hydrochloride (which could be separated by preferential coupling with 2-naphthol) and sulfonic acids of 1-amino-4-diazobenzene.

Sulfite Consumed.—Excess of hydrochloric acid was added to 50-cc. portions of original solution and the liberated sulfur dioxide distilled into standardized iodine solution: 9.00, 9.10 and 9.17 cc. of a normal solution being reduced, an average of 9.07 cc., corresponding to 90.7 cc. of normal sulfite solution in the original. Since 490.3 cc. was present before cleavage, the difference, 399.6 cc. of a normal solution (0.5 M) was consumed in reacting with one-tenth mole of dye. Quite accurately, two moles of sulfite reacted with one mole of dye.

Sulfate Formed During Cleavage.—Addition of mineral acids to the solution of cleavage products would have caused formation of sulfuric acid through hydrolysis of N-sulfonic acids. The sulfate formed during cleavage was therefore isolated from the ammoniacal solution as barium sulfate: 0.0280 g, of barium sulfate was found in 25-cc. portions of solution, which corresponded to 0.56 g. for the original solution, or to 4.8 cc. of normal sulfite solution that had been oxidized to sulfate during cleavage. Of the 399.6 cc. of sulfite solution, all but 1.2% remained in combination with cleavage products of the dye.

Distribution of Combined Sulfite between the Two Dye Components.—Conclusions could now be drawn regarding the probable composition of the reaction products; 0.78 equivalents of the primary component had been isolated, as free aniline. Two molar equivalents of sulfite (minus 1.2%), therefore, remained in combination with one full equivalent of 1-amino-4-phenol, and 0.22 equivalent of aniline. The solution contained N-mono- as well as N-disulfonic acids. Free 1-amino-4-phenol could not be detected. All of the secondary component was combined with at least one molecule of sulfite. If a single dye molecule combined with two molecules of sulfite, free aniline being formed as a result, both sulfite molecules must have attached themselves to the nitrogen atom of the secondary component. Conversely, since no free aminophenol had been formed, no N-disulfonic acid of the primary component could have been formed either. Disregarding the small amount of sulfate formation, one mole of dye should have yielded, approximately, 0.22 mole of an N-sulfonic acid of aniline, 0.22 mole (or slightly more) of N-monosulfonic acid of 1-amino-4-phenol and 0.78 mole (or slightly less) of an N-disulfonic acid of 1-amino-4-phenol.

Intramolecular Rearrangement and Hydrolysis of the N-Sulfonic Acids.—Two 50-cc. portions, boiled with an excess of hydrochloric acid to expel sulfur dioxide (residues from determinations of excess sulfite), were combined; an insoluble precipitate formed on cooling was isolated and dried over concd. sulfuric acid; a 100-cc. portion yielded 2.055 and 2.029 g., 0.1 mole of dye gave an average of 10.21 g. of substance. It showed the same characteristics, crystal habit, solubility, etc.. as the 1-amino-4-phenol-5-sulfonic acid.[6]

Anal. Calcd. for $C_6H_7O_4NS$: N, 7.40; S, 16.93; acidity, 1.0000 g. equiv. to 5.29 cc. of 1 N NaOH. Found: N, 7.39; S, 16.86; acidity, 1.0000 g. equiv. to 5.30 cc. of 1 N NaOH (phenolphthalein). The yield, 10.21 g., corresponded to 0.54 mole of I-amino-4-phenol-5-sulfonic acid per mole of dye.

Aniline, Originating through Hydrolysis of Its N-Sulfonic Acid.—The filtrate and wash liquor of the insoluble aminophenolsulfonic acid contained aniline, originating through decomposition of its free N-sulfonic acid. Two residual filtrates from the last-mentioned determination were combined, representing thus a 200-cc. portion of the original. The solution, after neutralization with sodium hydroxide, was evaporated

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[6] Post, *Ann.*, 205, 46 (1880).

to a smaller volume in a distilling flask. The aniline entrained was absorbed in dilute sulfuric acid and diazotized, 7.2 cc. of 1 N nitrite solution being required, corresponding to 18.0 cc., or to 0.018 mole of aniline per tenth mole of dye. 0.078 mole of anilime had been accounted for as a primary cleavage product; 0.096 mole, or 96%, of the primary dye component, therefore, was ultimately recovered as unchanged aniline.

Soluble 1-Amino-4-phenol-sulfonic Acid.—The distillation residue, free from traces of aniline or of aniline sulfonic acids, contained an aminophenol derivative of extraordinary solubility. By determining the amount of sulfuric acid formed through hydrolysis of N-sulfonic acids, it could be shown that the soluble product was a monosulfonated derivative of 1-amino-4-phenol. Its solution, again acidified with an excess of hydrochloric acid, required 17.8 cc. of 1 N nitrite solution for diazotization, corresponding to a total yield of 0.45 mole per mole of dye. The yield of this product, together with a yield of 0.54 mole of 1-amino-4-phenol-5-sulfonic acid, accounted for practically all of the secondary component of the dye. The diazonium compound of the soluble product showed similar characteristics as the 1-diazo-4-hydroxybenzene-5-sulfonic acid. It coupled with active azo components such as 1-naphthylamine, m-phenylenediamine, resorcinol, et~. Dyed upon untreated wool these dyes yielded shades which differed from those of corresponding azo derivatives of 1-amino-4-phenol-5-sulfonic acids by a noticeably greater tendency toward absorption in regions of longer wave lengths. Thus the dye containing 1-amino-8-hydroxynaphthalene-3,6-disulfonic ("H") acid as secondary component, gave clear bluish violet shades; the corresponding aminophenol-5-sulfonic acid derivative carmine red shades.

The dye containing 1-naphthylamine as secondary component was insoluble in the form of its free acid. It could be quantitatively isolated and was freed from impurities such as salts by thorough washing.

Anal. Calcd. for $C_{16}H_{13}O_4N_3S$: N, 12.25; S, 9.32. Found: N, 12.18; S, 9.34.

Identification of the Soluble Aminophenol Sulfonic Acid.—Since the product differed decidedly from the 1-amino-4-phenol-5-sulfonic acid, it was at first surmised that it was identical with the only other isomeric, nuclear, sulfonic acid, the 6-sulfonic acid. For comparison, the latter compound was prepared by two different methods.[7] The products thus obtained, identical with each other, were decidedly soluble in hot water but very little so at room temperature. They yielded azo dyes which were more soluble than corresponding dyes of the 5-sulfonic acid. The isomeric dyes did not differ visibly in color reactions or dyeing shades. The two sets differed perceptibly, however, from corresponding azo derivatives of the unknown substance. The possibility that the sulfonic acid group occupied the 2-, 3-, 5- or 6-position of the 1-amino-4-phenol nucleus was therefore excluded; it could exist only in combination with either the amino or the hydroxyl group. The formation of sulfonated, and distinctive azo derivatives excluded the first of these possibilities, leaving as the only remaining alternative conclusion that the product in question was a sulfonic ester of 1-amino-4-phenol, $H_2NC_6H_4OSO_3H$, a compound which apparently has not been observed previously, and which should also occur among the end-products of the sulfite reduction of nitro and nitrosophenol. The stability of this product in the presence of mineral acids seemed surprising in view of the comparative instability of the unsubstituted phenolsulfonic acid.[8] The compound hydrolyzed, apparently completely, when heated with about 5 *N* hydrochloric acid, at 90 to 93°, for eighty hours. The nuclear sulfonic acids of 1-amino-4-phenol proved perfectly stable under parallel conditions. Attempts to isolate the soluble compound as a potassium, barium or lead salt proved fruitless.

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[7] German Patents 150,982 and 160,170.

[8] Baumann, *Ber.*, 9, 1715 (1876); 11, 1907 (1878).

Boiling of its solution with alkalies, even with lead monoxide, caused destruction or displacement of the aromatic amino group.

The conditions under which hydrolysis and rearrangement of N-sulfonic acids proceeded were so chosen as to produce stable end-products in the most rapid manner (at 100° and a few minutes of boiling). Under slightly milder conditions hydrolysis proceeded more slowly. Portions of the original solution were heated to 90° and hydrochloric acid was added. On cooling the difficultly soluble 1-amino-4-phenol-5-sulfonic acid crystallized out and was isolated. Determination of sulfuric acid in solution yielded notably smaller amounts than were found previously, indicating the presence of disulfonic acids of aminophenol. On diazotization at 0° and subsequent coupling with azo components, derivatives of the aminophenol-sulfonic ester were obtained. Presumably, then, the disulfonic acid present before diazotization still possessed a sulfonic acid group attached to the nitrogen atom. The reaction (as well as yield figures) indicated that part of the N-disulfonic acid rearranged to form 1-amino-4-phenol-5-sulfonicacid, part of it to form the aminophenol-sulfonicester described above.

Cleavage of 4-Hydroxyazobenzene at Higher Temperatures.—Cleavage of the dye proceeded more rapidly at higher temperatures. The reagents, in the same proportions as before, were heated at 130 to 135°, in a small steel autoclave. Cleavage was complete after fifteen hours. Determination of molar ratio of reagents of primarily formed aniline gave practically the same results as were found in preceding experiments. A greater amount of sulfate, from 12 to 15% of the sulfite consumed, was formed. Since no trace of free aminophenol could be found, the formation of sulfate did not coincide with formation of greater amounts of totally unsulfonated products, but must have occurred at the expense of the N-*di*sulfonic acid yield. Hydrolysis and rearrangement, under the influence of acids, gave the same final reaction products as before. The yield of 1-amino-4-phenol-5-sulfonic acid was smaller; that of the aminophenol-sulfonic ester, however, correspondingly larger.

Sodium and Potassium Sulfite as Reagents.—Interaction between sodium or potassium sulfite and 4-hydroxyazobenzene was exceedingly slow below 100°, but went to completion in reasonable time at higher temperatures, requiring, for example, fifty hours of heating at 145 to 150". The reaction proceeded as with ammonium sulfite. As before, higher temperatures caused an increase in sulfate formation.

Cleavage of 4-Hydroxyazobenzene-4-sulfonic Acid, Na-Salt.—30.1270 g. of dye, exactly 0.1 mole, and 320 cc. of ammonium sulfite solution, equivalent to 490.3 cc. of 1 N solution, were heated under the same condition as described before, at 90 to 93°. Cleavage in this case was complete after eighteen hours. The decolorized solution was made up to volume and analyzed as previously described: 401.4 cc. of 0.5 M ammonium sulfite was consumed; 2.007 moles of sulfite reacted with one mole of dye. Ammonium sulfate formed during cleavage was equivalent to 0.6843 g. of barium sulfate, or to 5.6 cc. of normal sulfite solution, 1.4% of the sulfite consumed. An aliquot portion was freed of sulfite, acidified and diazotized with 1 N nitrite solution. A total of aromatic amines corresponding to 199.7 cc. of nitrite solution was found present, or practically the theoretically possible limit.

The addition of sodium chloride to the solution of cleavage products caused precipitation of sodium sulfanilate, which was identified by its crystal form. An exact quantitative estimation of primarily formed sulfanilate could not be made. Undoubtedly by far the greater part of the primary dye component was regenerated in its original form, as a result of cleavage.

An excess of hydrochloric acid was added to a portion of the original solution at 90 to 95°. The final useful products were sulfanilic acid (quantitative regeneration of the primary dye component), 1-amino-4-phenol-5-sulfonic acid (0.54 mole per mole of dye) and the extremely soluble 1-amino-4-phenol-sulfonic ester (0.46 mole per mole of dye). The yield ratio of the latter two products was identically the same as obtained in the cleavage of the unsulfonated dye.

Cleavage of 4-Hydroxyazobenzene-4-sulfonic Acid at 140 to 145°.—The sodium salt of the dye and sodium sulfite solution of approximately 0.75 M concentration were heated in a steel autoclave at 140 to 145°. At the end of twenty hours cleavage was found complete. Analytical determinations yielded very nearly the same results: 3.6% of the consumed sulfite was changed to sulfate, a little more than was formed at the lower temperature.

Summary

1. A new type reaction of monoazo dyes has been observed. They combine with two moles of a neutral sulfite, in solution, suffering cleavage into a primary amine and the salts of N-sulfonic and N-disulfonic acids.

2. 4-Hydroxyazobenzene yielded approximately 0.78 mole of aniline, 0.22 mole of an N-sulfonic acid of aniline, 0.78 mole of an N-disulfonic and 0.22 mole of an N-monosulfonic acid of 1-amino-4-phenol and no trace of unsulfonated aminophenol.

3. 4'-Hydroxyazobenzene-4-sulfonic acid reacted similarly, sulfanilate being formed as a result of cleavage.

4. Hydrolysis and rearrangement of free N-sulfonic acids resulted in complete recovery of the primary dye component in its original form; the secondary component yielded 1-amino-4-phenol-5-sulfonic acid and an extremely soluble, stable 1-amino-4-phenol-sulfonic ester, a compound not previously reported.

5. An explanation of the cleavage reaction has been suggested, founded on an assumption of functional differences between the two nitrogen atoms of the azo group.

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

STUDIES ON THE POLYMETHYLBENZENES. I. A STUDY OF THE JACOBSEN REACTION WITH PENTAMETHYLBENZENE, AND THE PREPARATION OF PREHNITENE[1]

BY LEE IRVIN SMITH AND ALBERT R. LUX

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I. Introduction and Historical

In 1887 Oscar Jacobsen[2] discovered that pentamethylbenzene when treated with concd. sulfuric acid undergoes a rather curious reaction in which a methyl group migrates from one molecule to another, leading to hexamethylbenzene and a tetramethylbenzene, prehnitene (1,2,3,4-),

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[1] Abstracted from a thesis by Albert R. Lux, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Jacobsen, *Ber.,* 20, 896 (1887).

which appears in the form of its sulfonic acid. This reaction is expressed by Jacobsen as follows

$$2C_6H(CH_3)_5 + H_2SO_4 \longrightarrow C_6(CH_3)_6 + C_6H(CH_3)_4SO_3H + H_2O$$

Jacobsen extended this reaction to other alkylated benzenes and found that it also took place with durene,[3] giving pentamethylbenzene and two trimethylbenzene-sulfonic acids, and with penta-ethylbenzene,[4] which gives hexa-ethylbenzene and the sulfonic acid of 1,2,3,4-tetra-ethylbenzene. Jacobsen also found that analogous reactions occurred when some of the halogenated benzenes were treated with concd. sulfuric acid, only in these cases it is the halogen which migrates instead of the alkyl group. Thus monobromodurene[6] gives dibromodurene and durene, the latter, of course, reacting at once to give higher and lower methylated benzenes.

The hexa-substituted benzenes obtained in these reactions are apparently end products and are stable toward sulfuric acid, even after several months' contact. In the case of the methylated benzenes, the reaction appears to be limited to the tetra- and pentamethylbenzenes, for the trimethylbenzenes are simply sulfonated by concd. sulfuric acid without any rearrangement; but in the case of the halogenated benzenes, even monobromobenzene will rearrange when treated with sulfuric acid, giving dibromobenzene and (presumably) benzene,[5] dibromobenzene giving tetra- and hexabromobenzene, and tribromobenzene giving hexabromobenzene. Similar migrations of halogens have been noted in the case of iodobenzene, o- and p-iodotoluene and o- and *p*-iodophenol.[6]

It has long been known that anhydrous aluminum salts will cause alkyl groups to migrate, not only into different positions in the same molecule but also from one molecule to another, but sulfuric acid is not frequently a reagent which causes migrations of this sort to take place. For this reason we were interested in *a* study of the Jacobsen reaction and we selected pentamethylbenzene as the object of our first study for two reasons: first, pentamethylbenzene when it undergoes the reaction gives fewer products than any other methylated benzene and, second, the tetramethylbenzene obtained in this way from pentamethylbenzene is prehnitene (1,2,3,4-), a very rare hydrocarbon, and we hoped to discover the conditions which would enable us to use the Jacobsen reaction with pentamethylbenzene as a method for making prehnitene in quantity. The work reported in this paper represents the preliminary investigation of a problem which has for its object: (1) verification of the facts as stated by Jacobsen, (2) determination of the limits of the Jacobsen reaction, and any special conditions which influence the reaction, (3) determina-

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[3] Jacobsen, *Ber.*, 19, 1209 (1886).

[4] Jacobsen, *ibid.*, 21, 2814 (1888).

[5] Jacobsen, *ibid.*, 20, 2837 (1887).

[6] Herzig, *ibid.*, 21, 664 (1888); Neumann, *Ber.*, 20, 581 (1887); *Ann.*, 241, 33 (1887).

tion of the mechanism of the reaction and (4) determination of the conditions under which the reaction can be run with pentamethylbenzene to give a good yield of prehnitene.

II. Method of Procedure and Discussion of Results

The procedure, from the initial materials to the final products, may be divided into four steps: (a) the Jacobsen reaction proper, (b) isolation of the products, (c) separation and purification of the products and (d) conversion of the prehnitene-sulfonic acid into prehnitene, together with the purification of the crude hydrocarbon. Each step in this procedure was examined, varying conditions as much as possible and determining the effects of these variations upon the yields of the products.

(a) The Jacobsen Reaction Proper.—The three variables studied in this step were the amount of sulfuric acid, the time and the temperature. The last two of these depend upon each other, for the same results are obtained by heating for a short time as are obtained by standing at room temperature for a longer time. In order, therefore, to standardize the procedure, we ran all of our experiments at room temperature, merely varying the time of standing. From the data in the table it is apparent that twenty-four hours is a sufficient time and that no improvement in the yield of products results on longer standing. The amount of sulfuric acid is also of little consequence as far as the final products are concerned, provided enough is used to react according to Jacobsen's equation, but it is more convenient to use more than this amount in order to get a thorough contact between the acid and the solid hydrocarbon.

(b) Precipitation of the **Sulfonic** Acid from the Sulfuric Acid Solution.—This is accomplished by adding ice to the solution; the variables in this step are the amount of ice added and the rate at which it is added, since this controls the temperature. The amount of ice used--enough to dilute the original acid to 50% by volume—was decided on the basis of the different yields of sulfonic acid obtained by using different amounts of ice. In order to avoid charring and the formation of tars, this ice must be added slowly and the mixture cooled in a bath of ice and salt.

(c) Separation and Purification of the Products.—The precipitate which forms when the sulfuric acid is diluted consists of hexamethylbenzene, prehnitene-sulfonic acid and tars. The separation of this mixture into its constituents is fairly easy, and is given in the experimental part.

(d) Conversion of Sodium Prehnitene-sulfonate into Prehnitene and Purification **of** the Hydrocarbon.—The hydrolysis of sulfonic acids to hydrocarbons in the presence of mineral acids has been studied by a number of investigators, but the most systematic investigation appears to be that of Armstrong and Miller,[7] who found that the reaction depends

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[7] Armstrong and Miller, *J. Chem. Soc.*, **45**, **148** (**1884**).

primarily upon the temperature and that any mineral acid can be used, provided means are available for obtaining high enough temperatures. These temperatures are all rather critical for given sulfonic acids, and are, in general, in the range of 120–200°—too high for hydrochloric acid unless autoclave conditions are employed. For this reason we chose sulfuric acid as the mineral acid, for any temperature up to the boiling point of sulfuric acid may be obtained by varying the concentration of the acid. Preliminary experiments showed, however, that the sulfonic acid of prehnitene (and also of other highly methylated hydrocarbons) is not only hydrolyzed by hot sulfuric acid but that other decompositions occur, leading to large amounts of tars from which no hydrocarbon can be obtained, and that the formation of these tars is largely a function of the time the sulfonic acid remains in contact with the hot sulfuric acid. Consequently, the only feasible method of hydrolysis appeared to be a "flash" system, in which the sulfonic acid was dropped slowly into hot sulfuric acid and the hydrocarbon distilled out immediately. Such a flash system gave beautiful results when applied to the hydrolysis of durene-sulfonic acid, yielding almost the quantitative amounts of durene; but prehnitene-sulfonic acid is exceedingly sensitive to the hot sulfuric acid and it requires very careful manipulation to get a good yield of hydrocarbon in this way. It was finally discovered, however, that if instead of the sulfonic acid, a water solution or paste of the sodium salt were used, good results could be obtained. The procedure finally developed consisted in passing superheated steam through sulfuric acid, holding the temperature of the acid at 145 to 150° by means of an outside bath, and then running in slowly a paste of the sodium salt of the sulfonic acid at such a rate that the temperature did not fall below 140 or rise above 155°. In this way the yield of hydrocarbon from the sodium sulfonate often runs as high as 90% and the average of a large number of runs is well over 80%. The temperature of hydrolysis is quite critical; below 140° the reaction is very slow, while above 160° there is much decomposition with charring and evolution of sulfur dioxide.

Experimental Part

The Jacobsen Reaction.—One typical run will be described in detail and others are summarized in the table. One-half mole (74 g.) of pentamethylbenzene (m. p. 52° or higher) is heated to 65° and to the resulting oil is added, with vigorous stirring, 200 cc. of concd. sulfuric acid which is at room temperature. By this procedure the hydrocarbon is cooled below its melting point and crystallizes in a finely divided form. This is essential, for if lumps of solid form they are quickly coated over with sulfonic acid or other material and the interior is protected completely against the sulfuric acid. After adding all of the acid, the resulting mush of white crystals and reddish liquid is placed in a cooling bath until it reaches room temperature, after which it is allowed to stand.

After standing for the requisite length of time, the mixture is cooled to 0° in a bath of ice and salt and 165 to 200 g. of cracked ice added in three portions, with vigorous stirring, making certain that the ice and water touch all parts of the mixture. This can be told by the disappearance of the dark reddish-brown color wherever the water touches the solid. After all of the ice has been added, the mixture is cooled to 0° and then filtered with suction through a cloth filter, pressing as dry as possible. The filtrate contains no appreciable amount of organic material and is discarded. The filter cake is leached out thoroughly with about 700 cc. of cold water and the resulting suspension is filtered. The precipitate is light brown and is hexamethylbenzene and by-products, while the red filtrate consists of a water solution of prehnitene-sulfonic acid also containing sulfuric acid.

The filtrate is worked up by converting the acids into the calcium salts by adding powdered calcium carbonate in small portions until there is no further effervescence. The precipitate of calcium sulfate is filtered off, washed thoroughly and discarded. The combined filtrates and washings contain the calcium salt of the sulfonic acid, which is converted into the sodium salt by adding concd. sodium carbonate solution as long as any calcium carbonate precipitates. The precipitate is filtered off, washed with water and discarded, after which the filtrate and washings are evaporated to dryness on the steam-bath, leaving the solid sodium salt of prehnitene-sulfonic acid; weight, about 40 g. or about 68% yield (assuming Jacobsen's equation to be correct). This sodium salt need not be purified before the hydrolysis to prehnitene, but for purposes of identification portions of it from several different runs were converted in the usual manner into the sulfone chloride, m. p. 73–75', and the sulfonamide, m. p. 187°.[8]

Purification of the Hexamethylbenzene.—The light brown precipitate of crude hexamethylbenzene weighs about 50 g. and melts gradually from 140 to 160°. It was purified by distillation under reduced pressure, 30 g. of distillate passing over at 170° under 80 mm. or 162' under 55 mm., and solidifying in the receiver to a white solid which, after recrystallizing once from a mixture of chloroform and alcohol, melts at 162'. A mixed melting point with a specimen of hexamethylbenzene, m. p. 162°, showed no depression. The yield, based on Jacobsen's equation, is 74%. The tarry residue remaining in the distilling flask weighed 20 g.

Conversion of the Sodium Prehnitene-sulfonate into Prehnitene, (a) Using Concd. Hydrochloric Acid.—About 10 g. of the sodium salt (or the sulfonic acid itself) was dissolved in 100 cc. of concd. hydrochloric acid. The solution was heated to the boiling point and steam passed through it for two hours. The distillate contained no oil, while the residue in the distilling flask was red and tarry. In another experiment 9 g. of the sulfonic acid was refluxed with 100 cc. of concd. hydrochloric acid for two hours and then distilled with steam. No trace of oil distilled over and the residue was very tarry.

(b) Distillation of the Sodium Salt with Ammonium Chloride.—Ten grams of dry sodium sulfonate was ground in a mortar with 50 g. of ammonium chloride, the mixture placed in a distilling flask and heated until the glass began to soften. In this case 1.5 g. of colorless oil distilled over, a yield of only 30%.

(c) Using Sulfuric Acid.—Preliminary experiments were carried out on the hydrolysis of durene-sulfonic acid to durene, as we could obtain this sulfonic acid in quantity from durene. These experiments indicated that it was necessary to heat, for very little durene is formed in the cold when the sulfonic acid is shaken with concd. sulfuric acid, contrary to the statement of Jacobsen.[3] By using 50% sulfuric acid and regulating the temperature very carefully, we finally found the conditions which would give a nearly quantitative yield of durene from the sulfonic acid, but when these condi-

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[8] Jacobsen, Ber., 19,1214 (1886); Kelbe and Pathe, *ibid.*, 19, 1552 (1886), however, give the m. p. of the amide as 177°.

tions were applied to prehnitene-sulfonic acid, only a 50% yield of hydrocarbon resulted. Moreover, if the temperature was increased, the yield diminished, and large amounts of tarry material resulted. After many experiments a procedure was developed which gave excellent results and which consists essentially of a "flash" hydrolysis and distillation with superheated steam. The flask in which the hydrolysis was conducted was an ordinary distilling flask of 500-cc. capacity, with two tubulatures in the bulb, one for carrying a thermometer, and the other for carrying a separatory funnel. The steam was superheated by means of a small superheater of copper tubing placed in the line. A typical experiment is described: the flask is charged with **100** cc. of water and immersed in an oil-bath at about **200'.** Then, with superheated steam passing through, concd. sulfuric acid is added through the dropping funnel until the temperature of the diluted acid in the flask reaches 150–160°. At this point a saturated water solution of **40** g. of the sodium prehnitene-sulfonate (or a thin paste of the solid and water) is run in at such a rate that the temperature of the acid mixture remains between **140** and **150'.** The hydrolysis takes place rapidly and the hydrocarbon is distilled out immediately by the current of steam. The oil distilling over is a very pale yellow and weighs **20** g. (88% yield based on the weight of the sodium sulfonate). On redistillation over 90% of the oil passes over within a range of 0.5°; b. p. **97** to 98° at **24–25 mm.**, and the distillate shows a freezing point of **−7.4".** (The freezing point of carefully purified prehnitene is −6.4°.)

Representative runs are shown in the table. The final run represents an experiment on a large amount of pentamethylbenzene to see whether or not the data obtained from small runs were applicable to larger quantities; the results show that prehnitene can be made in quantity by this method. It is, in fact, the only method for obtaining this hydrocarbon in any quantity, starting with materials which are themselves easily available.

TABLE I

SUMMARY OF THE RESULTS OF THE JACOBSEN REACTION WITH PENTAMETHYLBENZENE

Pentamethylbenzene, g.	Na sulfonate, g.	Crude prehnitene, g.	Crude hexamethylbenzene, g.	Pure hexamethylbenzene, g.	Time of standing, hours
74	45	15	..	..	24
74	40	20	50	30	24
74	35	20	49	30	48
74	45	16	49	..	48
74	40	21	55	..	48
74	45	18	41	34	24
74	35	18.5	45	..	24
74	46	17.5	48	..	24
74	40	19.5	50	..	24
74	37	20.0	50	..	24
74	43	18	55	30	24
1090	..	264	610	434	24

The Mechanism of the Jacobsen Reaction.—In this preliminary study most of the work was directed toward establishing the best conditions for carrying out the Jacobsen reaction in order that it might be used as a method for making prehnitene, and no extensive study of the mechanism of the reaction was made. In connection with another phase of this work, however, a sample of pentamethylbenzene-sulfonic acid was prepared and was placed in a desiccator over sulfuric acid for final drying. At the end of a week it was noticed that the acid had darkened quite a bit, and as the time went on, the color deepened. The sulfuric acid in the desiccator also darkened in color and sulfur dioxide was evolved, but this came from the sulfuric acid and not from the sulfonic acid above it. At the end of eight weeks both the sulfonic acid and the sulfuric acid were dark brown. The sulfonic acid (10 g.) was removed and worked up exactly according to the procedure used in carrying out the Jacobsen reaction. There resulted a brownish solid, insoluble in water or alkali, and an aqueous solution containing sulfonic acids.

The solid was sublimed, giving a white sublimate, m. p. 75 to 101°, which could not be purified because of the small amount. This m. p. is above that of pentamethylbenzene (52°) but below that of hexamethylbenzene (164°). However, some of the solid was mixed with pure hexamethylbenzene and the resulting mixture melted at 122–140°. Hence the solid is probably impure hexamethylbenzene and the impurity is most likely pentamethylbenzene resulting from hydrolysis of the sulfonic acid.

The sulfonic acids contained in the aqueous solution were converted into the sodium salts in the usual way and evaporated almost to dryness. A pasty mass of yellowish solid resulted; when this was hydrolyzed with sulfuric acid, there resulted 1.5 g. of oil in the distillate.

This experiment indicates that the first step in the Jacobsen reaction is a sulfonation and that it is the sulfonic acid, not the hydrocarbon, which rearranges, for the reaction will take place with the sulfonic acid alone in the absence of direct contact with sulfuric acid. Further study of this phase of the problem is in progress and will be reported later.

Summary and Conclusions

1. The rearrangement known as the Jacobsen reaction takes place essentially in the manner reported by Jacobsen, although there are considerable amounts of tarry by-products and Jacobsen's equation does not represent all that happens.
2. The optimum conditions for this reaction with pentamethylbenzene have been determined and when properly handled the reaction can be used as a method for making the rare hydrocarbon prehnitene (1,2,3,4-tetramethylbenzene) in quantity and with a yield of about 65% based on the pentamethylbenzene used. The yield of hexamethylbenzene is over 70%, while somewhat less than one-third of the original pentamethylbenzene is lost, principally as tars.
3. The hydrolysis of prehnitene-sulfonic acid to prehnitene has been studied in detail and a method is described which gives high yields of the hydrocarbon.
4. One experiment is reported which has a bearing upon the mechanism of the Jacobsen reaction.

MINNEAPOLIS, MINNESOTA

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

STUDIES ON THE POLYMETHYLBENZENES. II. THE MELTING POINTS OF THE TETRAMETHYLBENZENES, AND OF PENTA- AND HEXAMETHYLBENZENE, AND THE FREEZING POINT DIAGRAM OF MIXTURES OF DURENE AND XSODURENE

BY LEE IRVIN SMITH WITH F. H. MACDOUGALL

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The easiest method for preparing the polymethylbenzenes is by the direct methylation of commercial xylene[1] but at present the only pure polymethylbenzenes which can be isolated from the reaction mixture are durene, pentamethylbenzene and hexamethylbenzene. This is because alkylation, using the Friedel-Crafts reaction, yields all possible isomers, and while it is possible to separate by distillation the different steps in the alkylation, it is not possible to separate the isomers of the same step by this method. Durene (1,2,4,5-tetramethylbenzene) can, however, be made in this way because it has a relatively high melting point (80°) and can be frozen out of a mixture of its isomers containing relatively large proportions of it.

The yield of tetramethylbenzenes obtained by methylating xylene usually amounts to about 35% based on the xylene used, and contains about 4045% of durene. When this is frozen out, the filtrate contains all of the isodurene (1,2,3,5-) and prehnitene (1,2,3,4-), and this mixture is saturated, of course, with durene at the temperature of crystallization. This filtrate is at present useless as a source for isodurene and prehnitene because there is no known method by means of which the three tetramethylbenzenes can be separated from one another. The problem of this separation is now under investigation in this Laboratory, and the work reported in this paper deals with the preparation and (or) purification of each of the three tetramethylbenzenes, pentamethylbenzene and hexamethylbenzene, and a determination of their melting points and the freezing-point diagram for the system durene–isodurene, together with some thermodynamic considerations based upon these experimental data.

Preparation and Purification of Materials

1. Durene. Preparation[1] and Purification.—Eight hundred grams of crude durene was recrystallized four times by dissolving it in an equal weight of hot 95% ethyl alcohol, then cooling to 0°, filtering and washing with a little cold alcohol. After four recrystallizations, the durene weighed 500 g. This was then recrystallized once from 300 g. of thiophene-free benzene, yielding 430 g. The melting point of the durene (determined in the ordinary way, using a capillary tube and not correcting) rose slowly after each recrystallization until the fourth and fifth recrystallizations, which gave products having practically the same melting points (79.3–79.9° for the fourth, and

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[1] Smith and Dobrovolny, THIS JOURNAL, 48, 1413 (1926).

79.3–79.7° for the fifth). The sample to be used for accurate determinations was then placed in a vacuum desiccator over phosphorus pentoxide for two or three days.

2. Pentamethylbenzene. Preparation[1] and Purification.—Five hundred and fifty grams of crude pentamethylbenzene, m. p. 49–51°, was recrystallized four times from its own weight of 95% ethyl alcohol, followed by one recrystallization from 60% of its weight of thiophene-free benzene. The melting point rose progressively and was 51.5–53.0° for the fourth recrystallization and 52.2–53.1° for the fifth. The yield was only 127 g., as pentamethylbenzene is very soluble in benzene. The final sample was placed in a vacum desiccator over phosphorus pentoxide for a few days.

3. Hexamethylbenzene. Preparation[1] and Purification.—Three hundred and fifteen grams of hexamethylbenzene, m. p. 157–161°, was recrystallized from 400 g. of chloroform. The first and second crops were combined, as they showed practically the same melting point; yield, 270 g.; m. p. 162–164°. This product was then recrystallized three times by dissolving it in twice its weight of boiling chloroform, adding its own weight of hot 95% ethyl alcohol and cooling; yield at this point, 200 g. This product was then recrystallized once from its own weight of thiophene-free benzene; yield, 147 g.; m. p. 164.3–164.8°. The final sample was placed in a vacuum desiccator over phosphorus pentoxide for a few days.

4. **Isodurene, 1,2,3,5-Tetramethylbenzene.**—This compound has been previously made from bromomesitylene, methyl iodide and sodium,[2] but the yields are very poor. In addition to this method of synthesis, Jacobsen[3] reports a synthesis from mesitylene, methyl chloride and aluminum chloride, while Claus and Foecking[4] report a synthesis from mesitylene, methyl iodide and aluminum chloride; in view of the effect of aluminum chloride on aromatic hydrocarbons, it is very doubtful if these last two syntheses yielded pure isodurene.[6]

The method of preparation used in this work is new and it gives a good yield of product which is easily purified, as the crude product contains no isomeric substances. The synthesis starts with pure mesitylene and involves the reactions

$$C_6H_3(CH_3)_3\text{-}(1,3,5) + Br_2 \longrightarrow C_6H_2Br(CH_3)_3 + HBr$$
$$C_6H_2Br(CH_3)_3 + Mg \longrightarrow C_6H_2(CH_3)_3MgBr$$
$$C_6H_2(CH_3)_3MgBr + (CH_3)_2SO_4 \longrightarrow C_6H_2(CH_3)_4\text{-}(1,2,3,5) + (CH_3)(MgBr)SO_4\ (?)$$

Bromination of Mesitylene.—Six hundred and thirty-six grams (5.3 moles) of pure mesitylene (b. p. 58.3–58.5° at 15 mm.) is dissolved in 600–700 g. of carbon tetrachloride and the solution placed in a 3-liter flask provided with a reflux condenser, motor-driven stirrer and a dropping funnel, The flask is placed in a cooling bath, the stirrer is started and the mesitylene is brominated by running into it a solution of 900 g. of bromine in 900 g. of carbon tetrachloride (about 5% excess of bromine). The bromination requires about three hours but the rate at which the bromine is added is limited only by the efficiency of the condenser, as the reaction itself is quite rapid. Direct sunlight should not be allowed to strike the flask, as this increases side-chain bromination, although it is not possible to prevent some of this even in very dim daylight. After the bromination is completed, the reaction mixture is allowed to stand for an hour or so at room temperature. It will then have a light yellow or orange color. It is washed with water and then with alkali, after which the solvent is removed by distillation through a good

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[2] Jannasch, *Ber.*, **8**, 356 (1875); Bielefeldt, *Ann.*, **198**, 380 (1879); Jannasch and Weiler, Ber., **27**, 3442 (1894).

[3] Jacobsen, *ibid.*, **14**, 2629 (1881).

[4] Claus and Foecking, *ibid.*, **20**, 3097 (1887).

[5] See also Hofmann, ibid., **17**, 1915 (1884); Armstrong and Miller, *ibid.*, **16**, 2259 (1883); Orndorff and Young, *Am. Chem. J.*, **15**, 267 (1893).

column. The oil remaining in the distilling flask is dark and fumes when heated, and to remove side-chain halogen compounds it is boiled for an hour or two with a solution of 50 g. of sodium in a liter of 95% ethyl alcohol and then allowed to stand overnight. Unless this treatment with sodium ethylate is carried out, it is impossible to get a product which will not evolve hydrogen bromide on standing or on distillation.

The alkaline solution is diluted with much water, bringing the oily layer to the top by adding ether. The ethereal solution is washed thoroughly with water, separated, dried over calcium chloride and the ether then distilled off. The remaining oil is fractionated in *vacuo* using a good column. If enough sodium ethylate has been used in the purification, the product will not give any trace of precipitate with alcoholic silver nitrate on standing for twenty-four hours, if it is to be used in a Grignard reaction, it should meet this silver nitrate test. It is a colorless oil, b. p. 105–107° at 16–17 mm., 102.5–103.5° at 14 mm., m. p. -1 to $+1$°; yield, 800–900 g. (76 to 85%).

Grignard Reaction.—The apparatus consists of a 3-liter flask with 3 openings carrying a motor-driven stirrer, a dropping funnel and a reflux condenser, and provided with suitable calcium chloride guard tubes. In the flask are placed 48 g. of fine magnesium turnings,[6] 100 g. of bromomesitylene and 150 g. of ether, and the reaction is then started using the catalyst recommended by Gilman.[7] After the reaction has started. the stirrer is turned on and a solution of 298 g. of bromomesitylene in 600 g. of ether (total bromomesitylene. 398 g. = 2 moles) is added through the dropping funnel at such a rate that a brisk refluring continues. After all of the halogen compound has been added, the reaction mixture is refluxed on the steam-bath until practically all of the magnesium is dissolved. The flask is then cooled and a solution of 600 g. of dimethyl sulfate (freshly distilled in *vacuo*) in 400 g. of ether is run in through the dropping funnel with *vigorous* stirring until the amount of precipitated solid renders stirring useless. The reaction is quite vigorous and as the solid magnesium compounds separate out there is violent bumping. After adding all of the dimethyl sulfate (two to three hours), the reaction mixture is allowed to stand overnight and is then decomposed by adding excess dilute hydrochloric acid. The layers are separated and the ether layer is washed with water two or three times until the magnesium salts are removed, after which the excess dimethyl sulfate is destroyed by adding strong sodium ethylate *carefully* and boiling for an hour. The alcohol is then washed out with water, the ether solution dried over calcium chloride and the ether boiled off. The orange oil remaining is heated on the steam-bath for three to four hours with 25–30 g. of sodium shavings, after which it is filtered and then fractionated in *vacuo* using an efficient column.

The products of two such runs, when combined and fractionated, gave the following: I, b. p. up to 85° at 18 mm., 120 g.; II, b. p. 85–87° at 18 mm., 323 g.; III, b. p. above 87° at 18 mm. 10 g. (residue in the distilling flask). Fraction II is isodurene, with an almost constant boiling point of 86.5° at 18 mm. and a freezing point of -24.2 ± 0.1°. The yield is slightly over 60%. Fraction I consists of regenerated mesitylene, which may be brominated and used again. If the yield of isodurene is based upon the mesitylene used up in the reaction instead of the mesityleue taken, it runs about 80%.

Although the isodurene made in this way is quite pure, for purposes of determining physical constants it was refractionated through a long (4-foot) jacketed column,[8] separating the middle half, which was then refractionated, again separating the middle

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[6] Gilman and Mcyers, THIS JOURNAL, 45, 159 (1923); Gilman and Zoellner, *ibid.*, 50, 427 (1928).

[7] Gilman, *Rec. trav. chim.*, 47, 19 (1928): 46,463 (1927). The authors are greatly indehted to Dr. Gilman for private suggestions as to this procedure, and we take this opportunity of making acknowledgment.

[8] Peters and Baker, *Ind. Eng. Chem.*, 18, 69 (1926).

half. This gave one quarter of the original material having a constant boiling point of 84.6–84.7° at 17 mm.

5. **Prehnitene, 1,2,3,4-Tetramethylbenzene.**—This was prepared from pentamethylbenzene through the Jacobsen reaction, according to the directions given in the paper by Smith and Lux. Purification: 492 g. of crude prehnitene was washed twice with concd. aqueous sodium hydroxide, then once with water, dried over calcium chloride and fractionated through a 4-foot jacketed Peters column. The prehnitene fraction which resulted weighed 393 g. and had a constant boiling point of 97–98" at 24–25 mm. This was refractionated and the middle half collected (b. p. 97.2–97.6° at 24.5 to 24.8 mm., freezing point −6.9°, weight 186 g.). This product was again fractionated, collecting a middle portion of 132 g., b. p. 96.9 to 97.9' at 24 mm., freezing point −6.8'. As the recorded melting point of prehnitene is higher than this figure,[9] it was decided to attempt a further purification by converting prehnitene into the monobromo compound, purifying this by crystallization, and then regenerating the prehnitene through the Grignard reaction. One hundred and forty-five grams of prehnitene b. p. 98.9–99.0° at 26 mm., was brominated in chloroform, using the same procedure and proportions of materials as were given previously for the bromination of mesitylene. The product was washed with sodium ethylate and purified also according to the procedure used in the case of bromomesitylene. The yield of bromoprehnitene was 180 g. or 77%; b. p. 166–167° at 50 mm.; m. p. +24°. This material, recrystallized twice from its own weight of petroleum ether gave 110 g., m. p. 26.2–26.4°. Although the recorded m. p. of bromoprehnitene is +30°,[10] no further purification was attempted because the crystallization is accompanied by relatively large losses; 80 g. of this material was converted into the Grignard reagent using the procedure already outlined in the case of bromomesitylene. The Grignard reaction with bromoprehnitene does not run as smoothly, however, as it does with bromomesitylene, for after decomposing with acid the yield of prehnitene was only 28 g. (61%). This was boiled with sodium ethylate for two hours; the alcohol then was washed out, the oil heated with metallic sodium for two hours and then allowed to stand overnight, after which it was filtered and distilled. There resulted 23 g. of colorless, highly refractive oil, b. p. 66.5–66.8° at 4 mm., freezing point −6.9'. It is doubtful whether any effective purification is obtained as a result of this long process, for the freezing point of −6.9' is practically the same as that of the product obtained by three fractional distillations of the crude prehnitene from the Jacobsen reaction (−6.8'). In order, however, to be certain of the purity of the prehnitene, it was purified by converting it into the picrate[11] as follows: 69 g. of picric acid (0.3 mole) and 42 g. of prehnitene (slightly more than 0.3 mole; b. p. of the sample used, 100.0–100.5° at 27.5 mm., freezing point −7.7°) were mixed together in a beaker and heated on the steam-bath until most of the solid had dissolved. Then 200 cc. of hot 95% ethyl alcohol was added, everything brought into solution and the mixture cooled to 0°. The picrate crystallizes beautifully in the form of bright yellow stout needles, and after one recrystallization from its own weight of ethyl alcohol melts at 89.5 to 90.5'. The melting point depends somewhat upon the rate at which the bath is heated and also upon the length of time that the picrate is exposed to the air, for it slowly loses prehnitene, and as this happens the color fades and the melting point rises until, after standing for about a week, it reaches the melting point and color of picric acid. This undoubtedly explains the higher melting points given for the picrate by Töhl (92–95°) and by Schultz and Würth (92–96°). The yield of recrystallized picrate was 52 g., or about 50%, though the

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[9] Jacobsen, *Ber.*, 19, 1213 (18963; gives −4°; Töhl, *ibid.*, 21, 905 (1888), gives −5°.

[10] Töhl and Eberhard, *ibid.*, 25, 1526 (1892).

[11] Töhl, *ibid.*, 21, 905 (1888); Schultz and Worth, *Chem. Centr.*, 76, [1] 1443 (1905).

yield may be improved by using less alcohol in the preparation, as the second crop of crystals is as pure as the first. The picrate was decomposed by dropping it into an excess of concd. sodium hydroxide and steam distilling, when it gave practically the quantitative yield of prehnitene. The prehnitene is washed with alkali and then with water, dried and distilled. From 52 g. of pure picrate there resulted 17 g. of prehnitene and this, on distillation, gave 12 g. boiling at 75.0–75.5° (corr.) at 6.5 mm., and freezing at −6.4° (corr.).

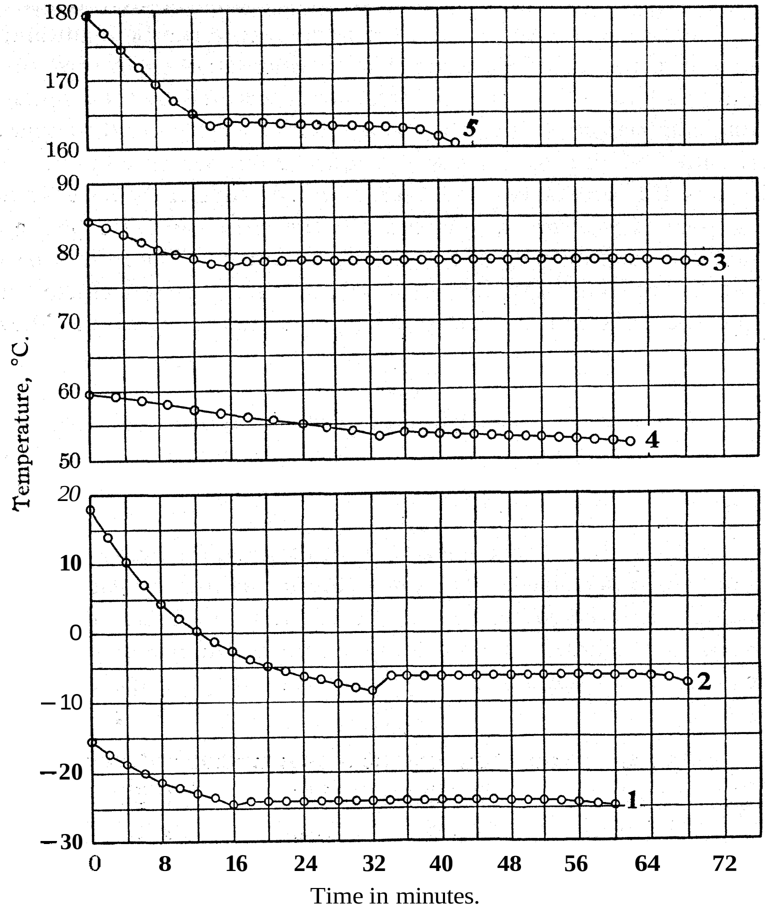

Fig. 1.—Cooling curves, freezing points of the polymethylbenzenes. **1**, Isodurene (1,2,3,5-); **2**, prehnitene (1,2,3,4-); 3, durene (1,2,4,5-); **4**, pentamethylbenzene; **5**, hexamethylbenzene.

Determination of Freezing Points.—The apparatus consisted essentially of the ordinary Beckmann Type for determining freezing points. The liquids used in the bath were water up to 100° and cottonseed oil for temperatures above 100°. For temperatures below that of the room, water and ice were used, while for temperatures below zero various freezing mixtures of ice and salt, ice and calcium chloride, or ice and hydrochloric acid were used. In a few cases carbon dioxide snow was used as the cooling agent, the temperature being limited by using as a bath a liquid freezing a few degrees below the freezing point of the sample. This procedure, however, is rather troublesome and does not have much advantage over a direct cooling bath of a freezing mixture, for with a little practice these freezing mixtures can be adjusted to almost any desired temperature and if a large enough bath is used, the temperature can be maintained for an hour without much difficulty. The thermometers used were all certified and in all cases the temperatures were corrected to total immersion. In taking the freezing points, the cooling curves were plotted, temperature against time, keeping the bath well below the temperature of the sample; in all cases the substances had been purified sufficiently so that at the freezing point there was a "plateau" in the curve and the temperature remained constant until all of the sample solidified. The results are given in Table I, together with the estimated accuracy, based chiefly on the length of the "plateau" in the freezing point curves, which are shown in Fig. 1.

TABLE I

CORRECTED FREEZING POINTS OF PURE POLYMETHYLBENZENES

Durene	79.28 ± 0.05°	**Pentamethylbenzene**	54.0 ± 0.1°
Isodurene	−24.0 ± 0.1°	**Hexamethylbenzene**	164.8 ± 0.1°
Prehnitene	− 6.40 ± 0.05°		

In much the same way the freezing point diagram for the system durene–isodurene was determined. The procedure in making up the sample was to start with a weighed amount of one of the pure constituents and add to it weighed amounts of the other, determining the freezing point of the mixture between each addition. There was always some supercooling,

TABLE II

FREEZING POINT DATA, SOLUTIONS OF ISODURENE IN DURENE

Mole fract. of durene	F. p., t°, °C.	Mole fract. of durene	F. p., t°, °C.	Mole fract. of durene	F. p., t°, °C.
100	79.28	62.68	57.41	25.23	18.75
94.04	76.27	65.76	52.21	21.35	10.19
88.76	73.47	49.90	47.47	17.26	2.50
84.00	70.86	45.40	43.35	16.00	− 3.17
79.40	68.30	41.70	39.69	14.00	−11.00
75.33	65.79	33.53	30.97	12.00	−16.35
68.70	61.55	28.85	23.53	10.00	−21.46

TABLE III

FREEZING POINT DATA, SOLUTIONS OF DURENE IN ISODURENE

Isodurene, mol. fr.	100.00	99.00	98.02	97.00	96.02	95.07	94.12	93.00	92.00
F. p., t°	−24.02	−24.51	−24.94	−25.45	−26.00	−26.46	−26.93	−27.55	−28.10

but no attempt was made to correct for the amount of material separating out and the freezing point of the mixture was taken as the highest point to which the thermometer rose after crystals once appeared. The data are given in Tables II and III, and are shown graphically in Fig. 2.

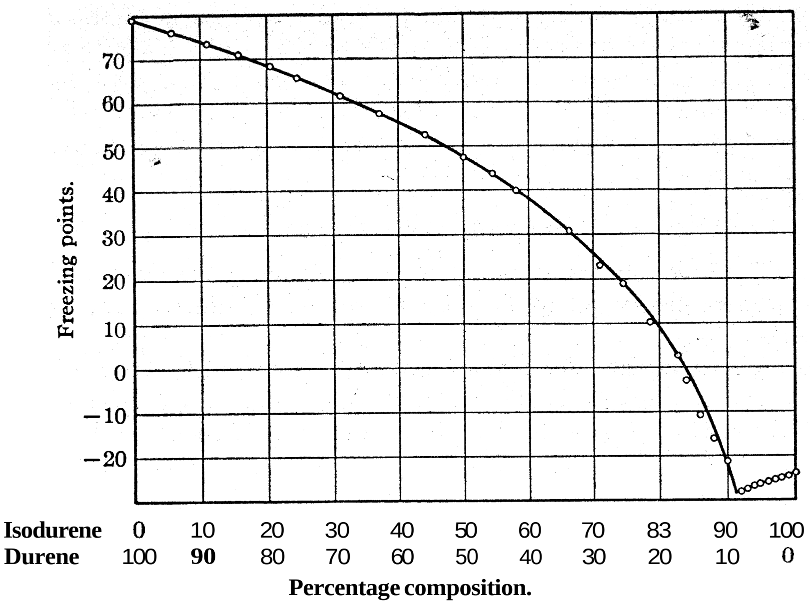

Fig. 2.—Freezing point diagram for the system durene-isodurene.

Discussion of the Results

A. Durene.—Assuming that durene and isodurene form an ideal liquid solution, at least over a certain range of concentrations, we obtain for the equilibrium constant, K_x (expressed in terms of mole fractions), the expression $K_x = x$ for the reaction

$$\text{Durene (solid)} \rightleftarrows \text{Solution of Durene}$$

where x is the mole fraction of durene in the solution. Hence we may write

$$\frac{d \log_e x}{dT} = \frac{L_f}{RT^2} \text{ or } \frac{d \log_e x}{d(1/T)} = -\frac{L_f}{R}$$

where L_f is the molar latent heat of fusion of durene. Making the substitution, $u = 1000\ (1/T - 1/T_0)$, where T_0 is freezing point of pure durene, and changing to ordinary logarithms, we obtain

$$L_f \text{ (in calories)} = -4574 \frac{d \log_{10} x}{du}$$

Over the range from 100% to about 66% of durene, it is found that the following equation represents satisfactorily the experimental data

$$-\log_{10} x = bu + cu^2$$

By the method of least squares, we find $b = 1.098$ and $c = 0.0993$. Hence

$$L_f = 4574\,(b + 2cu) = 5022 - 9.08 \times 10^5(1/T - 1/T_0)$$

For the temperature $T_0 = 352.38$, we find $L_f = 5022$ cal.

B. Isodurene.—The data for the freezing points cover the range from 100 to 92% isodurene with a maximum depression of the freezing point of only four degrees. An analysis of the results leads to the conclusion that liquid isodurene has a higher heat capacity than solid isodurene, but the accuracy of the measurements is not sufficient to enable us to make a more exact statement. The molar latent heat of fusion of isodurene turns out to be about 2550 calories.

Summary and Conclusions

1. The freezing points of all of the polymethylbenzenes containing four or more methyl groups have been determined, using carefully purified materials.
2. A new method for making isodurene in quantity is given.
3. The freezing point diagram for the system durene–isodurene has been studied, and from these data the latent heats of fusion have been calculated.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA]

1,6-ADDITION OF HYDROGEN TO UNSATURATED 1,4-DIKETONES

BY ROBERT E. LUTZ

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It is well known that conjugated systems of two or more multiple unions ending in oxygen are reduced with remarkable ease as compared with simple isolated ethylenic or carbonyl double linkages.[1] Typical examples are to be found in the conjugated systems of 1,2-diketones such as benzil, unsaturated 1,4-dicarbonyl and dinitro compounds such as fumaric and o-phthalic acids, unsaturated 1,4-diketones and ketonic acids, quinones, vat dyes and o-dinitrobenzenes; and doubly unsaturated 1,6-dicarbonyl and dinitro compounds such as muconic and p-phthalic acids and *p*-dinitrobenzene. The reductions of these compounds are generally interpreted as 1,4-, 1,6- or 1,8-addition of hydrogen to the terminal oxygen atoms to give dienols which, if the reductions are irreversible, immediately rearrange into stable forms or undergo some other secondary reaction such as the loss of water. Dibenzoylethylene (I), for example, is assumed to undergo the following changes in the course of reduction to dibenzoylethane (III).

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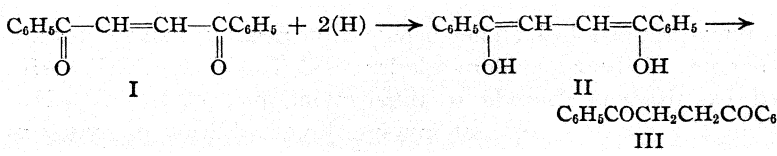
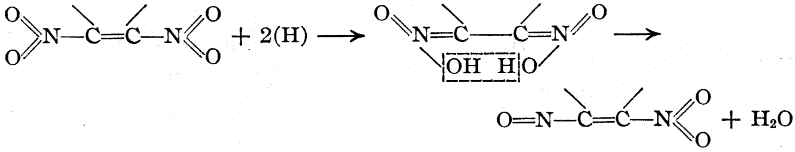
[1] Thiele, *Ann.*, 306, 87 (1899); 308, 333 (1899).



$$\underset{\mathrm{I}}{\mathrm{C_6H_5\underset{\underset{O}{\|}}{C}\!-\!CH\!=\!CH\!-\!\underset{\underset{O}{\|}}{C}C_6H_5}} + 2(\mathrm{H}) \longrightarrow \underset{\mathrm{II}}{\mathrm{C_6H_5\underset{\underset{OH}{|}}{C}\!=\!CH\!-\!CH\!=\!\underset{\underset{OH}{|}}{C}C_6H_5}} \longrightarrow \underset{\mathrm{III}}{\mathrm{C_6H_5COCH_2CH_2COC_6H_5}} \qquad (1)$$

Physico-chemical studies on the strictly reversible reduction of quinones show that electrons and hydrogen add to the terminal oxygen atoms to give as the final product a stable dienol, the corresponding hydroquinone.[2] The irreversible reductions of open chain 1,4-dicarbonyl compounds obviously cannot be directly studied by these physico-chemical methods, but they have been formulated and classified on a moderately exact basis in terms of the reduction potentials of a series of soluble reducing agents.[3] The evidence accumulated in these studies, particularly as concerns the unsaturated 1,4-diketones, is entirely consistent with and best interpreted in terms of a theory of conjugate reduction,[4] but this evidence, although convincing, can hardly be looked upon as conclusive.

The primary formation of the dienols postulated in irreversible reduction has been indirectly demonstrated in a few cases. In the reduction of benzil under special conditions Thiele[5] was able to isolate derivatives of the hypothetical intermediate stilbenediol. In the reduction of *o*- and *p*-dinitrobenzenes to nitronitrosobenzenes, Meisenheimer[6] isolated derivatives of the hypothetical di-aci-nitro-dihydrobenzenes and thus showed convincingly that reduction begins with 1,6- and 1,8-addition of hydrogen to the terminal oxygen atoms of the conjugated systems.



(2)

It was the object of this study of the reduction of certain unsaturated 1,4-diketones to obtain, also, more definite and positive evidence of the actual formation of the intermediate dienols that are postulated by the theory.

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[2] Conant, Kahn, Fieser and Kurtz, Jr., This Journal, 44, 1382 (1922).

[3] Conant and Lutz, ibid., 45, 1047 (1923); 46, 1254 (1924); Conant and Pratt, *ibid.*, 48, 1036 (1926).

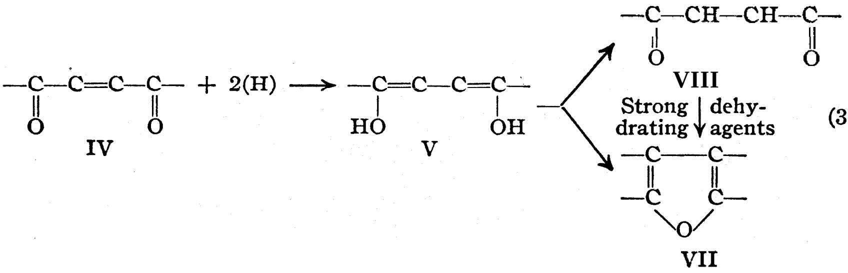
[4] The term "conjugated" is adequately defined as alternate, multiple and single unions, but so far as I am aware no general term has been applied to 1,4-, 1,6- and 1,8-additions which are peculiar to these systems. I shall therefore use the term "conjugate addition" and define it as addition to the ends of a conjugated system as distinct from simple addition to an individual multiple union either of that system or isolated. Conjugate reduction, then, is equivalent to conjugate addition of hydrogen.

[5] Thiele, Ann., 306, 142 (1899).

[6] Meisenheimer, *Ber.*, 36, 4147 (1903); Meisenheimer and Patzig, *ibid.*, 39, 2526 (1906).

Certain unsaturated 1,4-diketones behave in a peculiar manner toward reducing agents. Dibenzoyl-chloro-ethylene,[7] $C_6H_5COCH{=}CClCOC_6H_5$, is reduced by titanous chloride to dibenzoylethane, $C_6H_5COCH_2CH_2COC_6H_5$, but the reaction does not involve direct addition of hydrogen to the ethylenic double bond, as is shown by the fact that dibenzoyl-chloroethane, $C_6H_5COCH_2CHClCOC_6H_5$, is not reduced under these conditions and therefore is not an intermediate product. The chlorine must have been eliminated from some intermediate such as the dienol postulated by the theory of conjugate reduction.

It has been observed that the unsaturated 1,4-diketones, dibenzoylstyrene,[8] benzoyl-(trimethylacetyl)-styrene,[9] and dibenzoylmethoxyethylene,[7] are reduced under certain conditions to the corresponding triphenyl-, diphenyl-(*tert.*-butyl)- and diphenylmethoxyfurans; and that dibenzoylstilbene is reduced by zinc and acetic acid to a mixture of dibenzoyldiphenylethane and tetraphenylfuran.[10] These isolated reactions have not been adequately studied. The formation of the furans, however, suggests that the mechanism of the reaction involves the formation, just as in Equation 1, of an intermediate dienol (V) which can undergo one or both of two possible transformations, dehydration to the furan (VII), and rearrangement into the stable saturated 1,4-diketone (VIII).



(3)

No evidence has been obtained in the experiments cited to show that the saturated 1,4-diketone (VIII) is not directly formed in the reduction, and that it would not itself be dehydrated to the furan under the experimental conditions. Dehydration to the furan is a characteristic reaction of saturated 1,4-diketones of this type, and is usually interpreted as enolization followed by the loss of water from the intermediate dienol[11] (second

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[7] Conant and Lutz, This Journal, 47, 883 (1925).

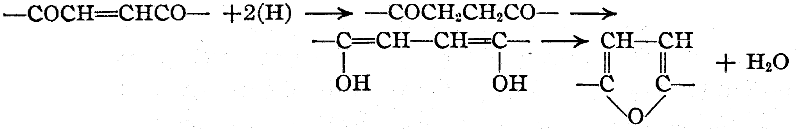
[8] Japp and Klingemann, *J. Chem. Soc.*, 57, 674 (1890); Japp and Burton, *ibid.*, 51. 430 (1887).

[9] Japp and Maitland, *ibid.*, 85, 1496 (1904).

[10] Zenin, Z. *Chem.*, 3, 313 (1876); *Jahresber. Fort. Thier-Chem.*, 409 (1875); Dorn, Ann., 153, 358 (1870); Magnanini and Angeli, *Ber.*, 22, 853 (1889).

[11] Smith, Ann., 289, 310 (1896); Knorr and Rabe, *Ber.*, 33, 3501 (1900); Borsche and Fels, *ibid.*, 34, 3877 (1906).

and third steps, Equation 4). This transformation can be brought about by a powerful catalytic and dehydrating agent such as sulfuric acid, or the hydriodic acid actually used in two of the reductions cited.[8,9] The general reaction, therefore, might be written not only as in Equation 3, but also as in Equation 4, where the assumed primary reduction product, the saturated 1,4-diketone, may be stable or may be partly or completely dehydrated to the furan under the conditions of the experiment.


(4)

Obviously it is important to know whether or not the saturated 1,4-diketones are stable under these various reducing conditions. If they are unstable and readily converted into the furans (as they would be with hydriodic acid as the reducing agent), then the formation of furans during reduction can have no bearing, either one way or the other, on the problem of mechanism, because reduction direct to the saturated 1,4-diketone (Equation 4) is thereby admitted as possible, and yet the possibility of the primary formation of a dienol (Equation 3) is by no means excluded. On the other hand, if reduction to the furans can be accomplished by reagents which have no dehydrating action upon the saturated 1,4-diketones, then the possibility of hydrogen adding directly to the ethylene double bond would be definitely excluded and the theory of conjugate reduction would be greatly strengthened.

In this research varied conditions have been found under which reduction of six unsaturated 1,4-diketones (Table I) takes place to give largely or exclusively the corresponding furan. In these six cases the corresponding saturated 1,4-diketones have been prepared and have been subjected to identical reducing conditions. In every case very little or no furan was formed and in most cases the saturated 1,4-diketones were largely or wholly recovered unchanged. Therefore, in these six cases, and by analogy in other related compounds, the saturated 1,4-diketones cannot be the primary intermediates in reduction (Equation 4), and the possibility of hydrogen adding directly to the ethylenic double bond is thereby definitely excluded. It would be difficult indeed to explain this formation of the

TABLE I

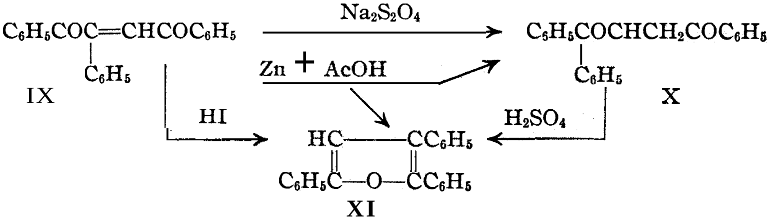
COMPOUNDS AND FORMULAS

1,2-Dibenzoylstyrene	$C_6H_5COC(C_6H_5)=CHCOC_6H_5$
1,2-Dibenzoylmethoxy-ethylene	$C_6H_5COCH=C(OCH_3)COC_6H_5$
1,2-Di-(4-chlorobenzoyl)-methoxy-ethylene	$ClC_6H_4COCH=C(OCH_3)COC_6H_4Cl$
1,2-Di-(4-bromobenzoyl)-methoxy-ethylene	$BrC_6H_4COCH=C(OCH_3)COC_6H_4Br$
1,2-Dibenzoylphenoxy-ethylene	$C_6H_5COCH=C(OC_6H_5)COC_6H_5$
1,2-Dibenzoyl-(4-methylphenoxy)-ethylene	$C_6H_5COCH=C(OC_6H_4CH_3)COC_6H_5$

furans on any other hypothesis than that the dienol, already predicted by the theory, was actually formed as an intermediate product (Equation **3**). Thus the theory of 1,6-addition of hydrogen to systems of this type seems to be strikingly confirmed.

Discussion of Results

Dibenzoylstyrene (IX) is reduced by zinc and acetic acid to a mixture of dibenzoylphenylethane (X) and triphenylfuran (XI), but under these conditions dibenzoylphenylethane, once formed, is stable and can be nearly quantitatively recovered unchanged in a test case. A much more powerful dehydrating agent (sulfuric acid) will convert it into the furan.[12]



IX X XI

On varying conditions and temperature the relative yields of ethane and furan are greatly altered. Zinc added to a boiling acetic acid solution of dibenzoylstyrene gave the furan in the larger amount; heating a mixture to boiling (reduction nearly complete before actually boiling) gave a larger proportion of the ethane; heating a similar mixture diluted with alcohol, or heating in alcohol with sodium hydrosulfite, yielded only traces of the furan; heating with sodium hydrosulfite in an alcohol–water mixture gave a practically quantitative yield of ethane, no furan being isolated. Thus the yield of furan depends on conditions and solvent, the two extremes being boiling acetic acid, which favors dehydration, and the alcohol–water mixture, which does not. These results are consistent with Equation **3** and the obvious prediction of the theory, namely, that the relative yields of ethane and furan are determined by the velocities of the two competing reactions, ketonization and dehydration of the intermediate dienol, and that these reaction velocities, particularly that of dehydration, are in turn dependent on temperature and solvent.

The methoxy derivatives of dibenzoyl-, di-(chlorobenzoyl)- and di-(bromobenzoyl)-ethylenes, $ArCOCH{=}C(OCH_3)COAr$ (Ar=aryl), were reduced with zinc and acetic acid to the corresponding methoxyfurans. In many of the experiments the corresponding methoxy-ethanes, $ArCOCH_2$-$CH(OCH_3)COAr$, were also obtained in appreciable yields; in other cases, although probably formed in small amounts, they were not isolated in a crystalline form.[13]

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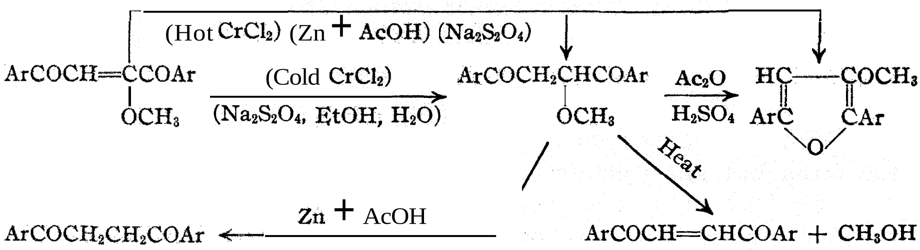
[12] Smith, J. Chem. *Soc.*, 57, 643 (1890).

[13] The methoxy-ethanes of this series are low-melting solids which crystallize ex-



The methoxy-ethanes, prepared by other methods, were subjected to reducing conditions identical with those under which the unsaturated compounds were converted partly or largely into the corresponding furans. They were not always completely stable. Nevertheless, a variety of reducing conditions were found under which the unsaturated 1,4-diketones gave the furans, yet under which the corresponding methoxy-ethanes were not appreciably dehydrated. In a few cases traces of the furan were isolated, produced by the dehydrating action of the solvent, acetic acid, on the saturated 1,4-diketones; but the yields were in no case significant. In the tests upon dibenzoyl-methoxy-ethane no attempt was made to recover the unchanged material because of the experimental difficulty involved,[13] but no appreciable conversion to the furan was observed (the furan is easily crystallized and significant amounts would have been found). In all of the other cases studied the bulk of the methoxy-ethanes was recovered unchanged and identified.

In many of the test experiments, particularly those carried out in acetic acid, small but definite amounts of the corresponding dibenzoylethanes, $ArCOCH_2CH_2COAr$, were produced by elimination of the methoxyl group. In one case a similar elimination of an aroxyl group was observed. The demethoxylated products were not obtained during reductions of the unsaturated 1,4-diketones where the furan was the sole or the main product. In qualitative tests it seemed that the methoxy-ethanes in the boiling solvents did not sufficiently decompose into the corresponding dibenzoylethylenes to account for the formation of the demethoxylated ethanes by reduction of this decomposition product. It would appear, then, that the methoxyl groups are directly reduced from the saturated methoxy 1,4-diketones.

The structures of the various products are shown by the transformations indicated above. The methoxy-ethanes in every case decompose on heating into the corresponding dibenzoylethylene and methyl alcohol,

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ceedingly slowly, particularly when they are obtained as oils and in a crude state. These properties explain why dibenzoylmethoxy-ethane was not obtained crystalline in an earlier investigation (ref. 7). In general these oils will stand for weeks before solidifying. Once well started crystallization occurs in from a few hours to several days or a week.

a reaction analogous to the easy elimination of water from β-hydroxy acids, and parallel with the decomposition of α-methoxy-β-(5-bromo-2,4-methoxybenzoyl)-propionic acid and its ester.[14] Two of the methoxy-ethanes are dehydrated by means of acetic anhydride and sulfuric acid to the corresponding furans. Dibenzoyl-methoxy-ethane does not yield the furan but undergoes some transformation not yet understood.

On the basis of the theory of conjugate reduction the factor governing whether or not reduction will occur is the potential of the reducing agent,[3] but the relative yields of furan and ethane should be independent of the nature and potential of the reducing agent,[15] except for specific catalysis of either of the two competing reactions, ketonization and dehydration. It is difficult to predict the extent of this possible catalytic effect, but it is probably concerned mainly with the hydrogen-ion concentration rather than with any specific effect of the reducing agent itself. However, I think it may be said that if the nature of the solvent and the temperature are not greatly altered (even if the hydrogen-ion concentration varies somewhat) different reducing agents should give results of the same order. Thus if sodium hydrosulfite reduced an ethylene to the furan, then in the same solvent and at the same temperature reduction by means of chromous chloride, and even by zinc and acetic acid (assuming its reducing action to depend on potential), ought to give comparable yields of the furan.

Experiments in boiling 95% ethyl alcohol on two methoxyethylenes show that chromous chloride, sodium hydrosulfite and zinc and acetic acid give in each case considerable and comparable yields of the furan. With chromous chloride the yield of furan was rather low, but as a certain amount of water was present in the reagent the discrepancy in relative yields is not significant. The experiments are thus in qualitative agreement with prediction and are consistent with the view that the second step in Equation 3 is independent of the nature of the reducing agent,[15] but is dependent on the nature of the solvent and its effectiveness in promoting dehydration. I hope to investigate this problem further.

The aroxy-dibenzoylethylenes, $C_6H_5COCH{=}C(OAr)COC_6H_5$, are easily reduced but usually only to the corresponding dibenzoyl-aroxy-ethanes. Reduction by zinc in boiling acetic acid and acetic anhydride, however, gives simultaneously the aroxy-ethanes and the furans; under these conditions the aroxy-ethanes are perfectly stable. Dibenzoyl-phenoxy-ethane decomposes into dibenzoylethylene and phenol on heating and can be readily converted by acetic anhydride and sulfuric acid into the furan.

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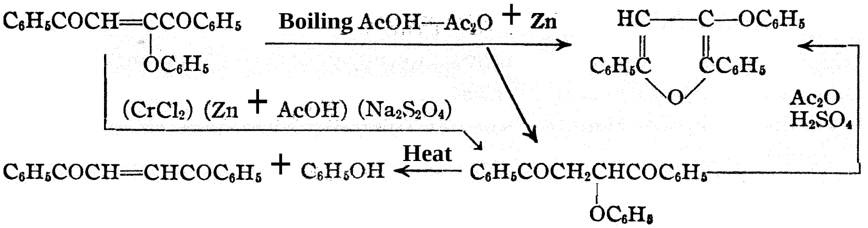
[14] Rice, THIS JOURNAL, 50, 229 (1928).

[15] I refer to the ordinary reducing agents as distinct from "hydrogenating" agents such as platinum and hydrogen, the action of which certainly cannot be expressed in terms of reduction potential [Conant and Cutter, *ibid.*, 44, 2651 (1922)]. Investigation of the catalytic hydrogenation of the unsaturated 1,4-diketones is now under way in this Laboratory.



The simple and aryl substituted dibenzoylethylenes, in marked contrast to those in which an ethylene hydrogen is replaced by methoxyl, aroxyl or phenyl, do not give furans on reduction under the conditions studied. Ethylenic substituents may be arranged in the following order of increasing tendency toward furan formation during reduction; hydrogen, halogen and 3-methylphenoxyl (no tendency), 4-methylphenoxyl, phenoxyl, phenyl and methoxyl. When, however, one benzoyl in dibenzoylstyrene is replaced with trimethylacetyl, no furan formation at all is observed under comparable conditions. Little significance can be attached to this series at present since distinction is not made between the two entirely different effects on the rate of ketonization and on the ease of dehydration.

It might be argued that these reductions of unsaturated 1,4-diketones are really 1,4-additions (they cannot be 1,2-additions). The large amount of information at hand (refs. 1–5) and the results of this investigation are not consistent with such a hypothesis; the theory of 1,6-addition is far more reasonable and involves fewer assumptions than 1,4-addition, particularly as concerns transformations of the intermediate products, affinity of oxygen for hydrogen and the mechanism of the reducing action of the reagents. Furthermore, dimolecular reduction products, though frequently obtained in the reduction of α,β-unsaturated ketones,[16] have never been reported in the extensive studies on unsaturated 1,4-diketones. In this investigation, however, a dimolecular product (m. p. 161°) was obtained in one case, namely, the reduction of dibenzoylethylene with zinc and acetic acid. A study of this reaction is being made and will be reported in detail in a later paper.

Conclusion

The conclusions of this investigation are based on the experimental observations that certain unsaturated 1,4-diketones are reduced under definite conditions to furans, that the saturated 1,4-diketones are not the primary intermediate products and that the saturated 1,4-diketones and the furans are independent end products of the reduction. These experimental results coincide exactly with the obvious prediction of the theory of conjugate reduction, namely, that the dienol (the hypothetical

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[16] Harries, *Ann.*, *296*, 285 (1897); see, also, Conant and Cutter, THIS JOURNAL, **48**, 1016 (1926).

intermediate both in reduction of unsaturated 1,4-diketones and in dehydration of saturated 1,4-diketones) can either rearrange or pass into the furan by the loss of water. Furthermore, these results can be explained reasonably only by assuming the intermediate formation of this dienol in the process of reduction. Therefore, although the dienol has not been and probably cannot be isolated and studied directly, the evidence so far accumulated points clearly toward its existence momentarily as the primary intermediate reduction product, and thus affords confirmation of the theory of 1,6- or conjugate addition of hydrogen to the unsaturated 1,4-diketones and related substances.

Certain of the preliminary experiments on dibenzoylstyrene were carried out by Mr. William B. Brown at New York University, as a part of Senior Research under the Department of Chemistry.

Experimental Part

Preparation of Methoxy Unsaturated **1,4-Diketones.**—The methoxy unsaturated 1,4-diketones were prepared by methods outlined in earlier investigations.[7,17] The following preparation of the di-(chlorobenzoyl)-methoxy-ethylene (new) illustrates the general procedure employed.

dl-**1,2-Di-(4**-chlorobenzoyl)-1,2-**dibromo**-ethane, $ClC_6H_4COCHBrCHBrCO-C_6H_4Cl$.—Seventy g. of di-(chlorobenzoyl)-ethylene (trans) was dissolved in hot chloroform and treated with a chloroform solution of 37 g. of bromine. The temperature was maintained at about 60° by the heat of reaction. On cooling 49 g. of nearly pure *meso*-dibromide[7] separated, and on evaporation of the solvent 49.5 g. of nearly pure dl-isomer was obtained. The total yield of dibromides was 92%. The dl-isomer (new) was recrystallized from alcohol and was more soluble than the *meso;* m. p. 124.5".

Anal. Calcd. for $C_{16}H_{10}O_2Cl_2Br_2$: Cl, Br, **49.53.** Found: Cl, Br, 49.78.

When bromine was added to 50 g. of the ethylene in glacial acetic acid, 55 g. of the *meso*-dibromide crystallized from the mixture and 18 g. of the dl-isomer was isolated from the filtrate (total yield, 95%).

These results correspond with those previously reported on other dihalides of dibenzoylethylene;[17] nearly equal yields of the two isomers were obtained using chloroform as the solvent at elevated temperature, but the product was largely *meso* when acetic acid was used. That the configurations are as I have assumed is evident by analogy to the mode of preparation and properties of the dihalides of dibenwylethylene the configurations of which are known.[18]

1,2-Di-(4-chlorobenzoyl)-methoxy-ethylene, $ClC_6H_4COCH{=}C(OCH_3)COC_6H_4Cl$.—Di-(chlorobenzoyl)-dibromo-ethane was treated in the usual way[7] with two equivalents of sodium methylate. The colorless product was recrystallized from alcohol; m. p. 130°; soluble in hot alcohol and in cold chloroform, benzene and acetone; insoluble in cold alcohol and petroleum ether.

Anal. Calcd. for $C_{17}H_{12}O_3Cl_2$: Cl, 21.23. Found: Cl, 21.30.

Preparation of Dibenzoyl-aroxy-ethylenes

Dibenzoylphenoxy-ethylene.—The method of preparation formerly used[7] involved the action of sodium phenolate in ether on dibenzoyldibromo-ethane. The procedure

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[17] Lutz, This Journal, 48, 2905 (1926).

[18] Lutz, *ibid.*, 49, 1106 (1927).

was altered. The sodium was first dissolved in absolute ethyl alcohol, treated with an excess of phenol and added to a suspension of dibenzoyldibromo-ethane in absolute ethyl alcohol. The method gave fair results and was rapid. Using m-cresol a mixture of two stereoisomers was obtained, analogous to the two di-(2,4,6-trimethylbenzoyl)-methoxy-ethylenes.[17] One new compound was prepared by this method, dibenzoyl-(3-methoxyphenoxy)-ethylene.

In a typical experiment 20 g. of phenol was added to a solution of 5 g. of sodium in 200 cc. of absolute ethyl alcohol. This solution was added to a suspension of 40 g. of dibenzoyldibromo-ethane in 160 cc. of absolute alcohol. The mixture was boiled for a few minutes and diluted with water. The gummy precipitate was crystallized from alcohol and gave 21 g. of nearly pure dibenzoylphenoxy-ethylene (63%).

A 62% yield of dibenzoyl-(4-methylphenoxy)-ethylene was obtained by this method using *p*-cresol instead of phenol.

1,2-Dibenzoyl-(3-methoxyphenoxy)-ethylene, $C_6H_5COCH{=}C(OC_6H_4OCH_3\text{-}m)\text{-}COC_6H_5$.—By the above method, using resorcinol monomethyl ether instead of phenol, a small yield (about 10%) of colorless crystals was separated from an oil and recrystallized from alcohol; m. p. 110°.

Anal. Calcd. for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 76.79; H, 4.93.

1,2-Dibenzoyl-(3-methylphenoxy)-ethylene (Low-Melting Isomer), $C_6H_5COCH{=}C(OC_6H_4CH_3\text{-}m)COC_6H_5$.—*m*-Cresol was substituted for phenol in the above reaction. The product obtained was partially separated by fractional crystallization from alcohol into the known dibenzoyl-(3-methylphenoxy)-ethylene (m. p. 103°),[7] and a stereoisomer. The latter, purified by repeated recrystallization from alcohol, was obtained as nearly colorless needles which melted at 95° to a pale yellow liquid. When crystallized slowly the high-melting isomer (103°) gave bunches of flat, thin, long, radiating, colorless needles. The low-melting isomer (95°) gave long thick prisms which had a very pale yellowish luster. The latter probably corresponds in configuration to the yellow isomer of di-(2,4,6-trimethylbenzoyl)-methoxyethylene.

Anal. Calcd. for $C_{23}H_{18}O_3$: C, 80.69; H, 5.30. Found: C, 80.70; H, 5.32.

Reduction of both isomers by means of (a) chromous chloride, (b) zinc and acetic acid and (c) sodium hydrosulfite gave nearly quantitative yields of the known dibenzoyl-(3-methylphenoxy)-ethane.[7] Zinc and acetic acid reductions failed to give appreciable amounts of a furan; in one case, however, a trace of dibenzoylethane was isolated.

Preparation of Reduction Products

1,2-Dibenzoylmethoxy-ethane, $C_6H_5COCH_2CH(OCH_3)COC_6H_5$.—A mixture of 2 g. of dibenzoylmethoxy-ethylene, 5 g. of sodium hydrosulfite, 20 cc. of alcohol and 12 cc. of water, was boiled for forty minutes and diluted with water. The precipitated oil was dissolved in methyl alcohol and cooled; 0.04 g. of diphenylmethoxyfuran separated. The filtrate was diluted with water and the precipitated oil was separated and allowed to stand for several weeks. It finally crystallized and 1.5 g. of crude product (m. p. 41–43°) was obtained. It was quite soluble in most organic solvents but was insoluble in petroleum ether. The product tends to precipitate as an oil which crystallizes exceedingly slowly. Recrystallization was accomplished by dissolving the substance in ethyl bromide, cooling and diluting the solution with petroleum ether until very slightly turbid. The mixture was then seeded and allowed to stand in an ice-bath for four to six hours, during which time more petroleum ether was added. Colorless crystals formed slowly and after two such operations melted at 48.5–49°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 77.25; H, 6.11. Found: C, 76.64; H, 6.08.

In a second experiment the time of heating was cut down to ten minutes; 1 g.

of furan was obtained from 10 g. of the ethylene. Since long heating does not appreciably affect the yield of furan, it follows that dibenzoylmethoxy-ethane, once formed, is stable and not appreciably dehydrated to the furan under these conditions.

Acetic anhydride and concd. sulfuric acid failed to dehydrate the ethane to the furan, but gave instead oils and a colorless solid which will be investigated further.

Decomposition of Dibenzoylmethoxy-ethane.—One-tenth gram **of dibenzoyl**methoxyethane was heated to 210–215° for twenty minutes. The molten mass turned yellow and decomposed with the evolution of a droplet of methyl alcohol which was collected and identified by conversion into the methyl ester of 3,5-dinitrobenzoic acid. The residue was crystallized from alcohol and gave 0.45 g. of dibenzoylethylene (identified by mixed melting point).

A small sample of dibenzoylmethoxy-ethane was boiled for a few minutes in an acetic acidanhydride mixture. The solution remained colorless and no evidence of decomposition was observed.

2,5-Di-(4-chlorophenyl)-methoxyfuran, $ClC_6H_4C{=}CH{-}C(OCH_3){=}C(C\ H_4Cl)O$.—A mixture of 14 cc. of glacial acetic acid, 1 cc. of acetic anhydride, 6 g. of zinc dust and 2 g. of di-(chlorobenzoyl)-methoxy-ethylene was brought to a boil, filtered and poured into water. The product was crystallized from alcohol; yield, 1.1 g.; m. p. 114°.

Anal. Calcd. for $C_{17}H_{12}O_2Cl_2$: Cl, 22.14. Found: Cl, 22.22.

1,2-Di-(4-chlorobenzoyl)methoxy-ethane, $ClC_6H_4COCH_2CH(OCH_3)COC_6H_4Cl$.—A mixture of 6 g. of di-(chlorobenzoyl)-methoxy-ethylene, 25 g. of sodium hydrosulfite, 120 cc. of alcohol and 30 cc. of water was boiled under a reflux condenser for twenty minutes, cooled and diluted with water. The resulting oil, after standing for several weeks, was induced to crystallize. It was purified by dissolving in enough warm methyl alcohol to prevent immediate precipitation as an oil on cooling to room temperature. It was then seeded and allowed to stand for one to two days to crystallize. The yield of nearly pure material (m. p. 58–59°) was 5.7 g. It was soluble in hot ligroin, petroleum ether and alcohol but insoluble cold, and soluble in cold acetic acid, benzene, chloroform and ether. It formed colorless granular crystals, m. p. 61.5°.

Anal. Calcd. for $C_{17}H_{14}O_3Cl_2$: C, 61.45; H, 4.25; Cl, 21.35. Found: C, 61.47; H, 4.14; Cl, 21.04.

A small sample was converted by the action of acetic anhydride containing a trace of sulfuric acid into di-(chlorophenyl)-methoxy-furan, which was identified by mixed melting points. The yield was low.

Decomposition of Di-(chlorobenzoyl)-methoxy-ethane.—Two-tenth gram **of di-**(chlorobenzoyl)-methoxy-ethane was heated for ten minutes at 200° in a suitable apparatus. Decomposition took place. A droplet of distillate was obtained and identified as methyl alcohol by conversion into the methyl ester of 3,5-dinitrobenzoic acid. The dark orange residue was crystallized from acetone and gave 0.05 g. of yellow crystals which were identified by mixed melting points as di-(chlorobenzoyl)-ethylene.

In a qualitative experiment a sample of di-(chlorobenzoyl)-methoxyethane dissolved in an acetic acid–anhydride mixture to give a colorless solution which remained colorless on boiling. Failure to develop a yellow color indicated that no decomposition into dibenzoylethylene occurred.

2,5-Di-(4-bromophenyl)-methoxy-furan, $BrC_6H_4C{=}CH{-}C(OCH_3){=}C(C_6H_4Br)O$.—A mixture of 1 g. of di-(bromobenzoyl)-methoxy-ethylene, 2 g. of zinc dust and 15 cc. of glacial acetic acid was brought to a boil. filtered and diluted with water. The product (0.82 g.) was recrystallized several times from alcohol and obtained as a mat of colorless needles melting at 113°

Anal. Calcd. for $C_{17}H_{12}O_2Br_2$: C, 50.01; H, 2.97; Br, 39.17. Found: C, 49.83; H, 3.01; Br, 39.45.

1,2-Di-(4-bromobenzoyl)-methoxy-ethane, $BrC_6H_4COCH_2CH(OCH_3)COC_6H_4Br$.—A mixture of 6 g. of di-(bromobenzoyl)-methoxy-ethylene, 120 cc. of alcohol, 30 cc. of water and 25 g. of sodium hydrosulfite was boiled for twenty minutes. On dilution with water an oil was obtained which was induced to crystallize after standing for several weeks. It was purified by dissolving in warm methyl alcohol, cooling, seeding and allowing to stand for twenty-four hours; yield, 4.5 g. The recrystallized product was colorless, melted at 72° and was soluble in benzene, acetone, ether and hot alcohol, and slightly soluble in cold alcohol.

Anal. Calcd. for $C_{17}H_{14}O_3Br_2$: C, 47.91; H, 3.32. Found: C, 47.93; H, 3.37.

Decomposition of **Di-(bromobenzoyl)-methoxy-ethane.**—Fifteen hundredths of a gram of di-(bromobenzoyl)-methoxy-ethane was heated to 210–220° for ten minutes. Decomposition took place and a droplet of methyl alcohol distilled and was identified as the methyl ester of 3,5-dinitrobenzoic acid. The yellow residue was dissolved in hot chloroform and 0.05 g. of yellow crystals was obtained and identified as di-(bromobenzoyl)-ethylene.

1,2-Dibenzoylphenoxy-ethane, $C_6H_5COCH_2CH(OC_6H_5)COC_6H_5$.—Reductions of 0.5 g. of dibenzoylphenoxy-ethylene by (a) chromous chloride and (b) sodium hydrosulfite gave, respectively, 0.47 g. and 0.49 g. of nearly pure dibenzoylphenoxy-ethane. The product was purified for analysis by recrystallizations from alcohol (m. p. 120°). Reduction of 1.65 g. of **dibenzoylphenoxy-ethylene** with zinc and acetic acid gave 0.9 g. of the ethane.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.99; H, 5.49. Found: C, 80.10; H, 5.77.

2,5-Diphenyl-3-phenoxyfuran, $C_6H_5\overline{C{=}CH{-}C(OC_6H_5){=}C(C_6H_5)O}$.—One gram of dibenzoylphenoxy-ethane was treated with acetic anhydride containing a drop of concd. sulfuric acid. Immediate reaction occurred accompanied by color formation. The mixture was decomposed in water and the product (0.9 g.) recrystallized several times from alcohol; m. p. 91°.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.57; H, 5.17. Found: C, 84.74; H, 5.12.

Decomposition of **Dibenzoylphenoxy-ethane.—A** sample of dibenzoylphenoxy-ethane was heated to 270°. A droplet of phenol distilled and was identified by its odor and conversion into tribromophenol. A good yield of dibenzoylethylene was obtained by recrystallizing the dark colored residue.

1,2-Dibenzoyl-(4-methylphenoxy)-ethane, $C_6H_5COCH_2CH(OC_6H_4CH_3)COC_6H_5$.—Dibenzoyl-(4-methylphenoxy)-ethylene was reduced by (a) sodium hydrosulfite and (b) zinc and acetic acid, to give in each case nearly theoretical yields of dibenzoyl-(4-methylphenoxy)-ethane, which was obtained after repeated crystallization from alcohol as colorless crystals melting at 108.5°.

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.18; H, 5.85. Found: C, 80.28; H, 5.84.

2,5-Diphenyl-3-(4-methylphenoxy)-furan, $C_6H_5\overline{C{=}CHC(OC_6H_4CH_3\text{-}p){=}C(C_6H_5)O}$.—One gram of dibenzoyl-(4-methylphenoxy)-ethane was dissolved in acetic anhydride containing a trace of concd. sulfuric acid. The mixture was decomposed with water and the product crystallized from alcohol; yield, 0.7 g.; m. p. (pure) 113°.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.60; H, 5.56. Found: C, 84.18; H, 5.59.

A Study of the Formation of Furans During Reduction of Unsaturated 1,4-Diketones

Methods of Reduction and Isolation of Products.—Three reducing

agents, sodium hydrosulfite, chromous chloride and zinc and acetic acid were used under different conditions in this research.

TABLE II

ACTION OF REDUCING AGENTS ON UNSATURATED 1,4-DIKETONES

Red. agent	Subs., g.	Solvent and conditions	Red. prods. and yields, %	Prods. from action of red. agents on corresponding satd 1,4-diketones, %
		Dibenzoylphenylethylene		
Zn + AcOH	1.0	4g. Zn + 15 cc. AcOH, Δ^a	Ethane, 44; furan, 29	Recov.[b] 93
	0.5	In 50 cc. Δ AcOH, add 1 g Zn	Ethane, 34; furan, 52	Recov. 95
	5.0	75 cc. 95% EtOH, 25 cc. AcOH, A1 h.	Ethane, 64; furan, 5.6	....
$Na_2S_2O_4$	[c]	95% EtOH, Δ1 h.	Mainly ethane; furan, 2	....
	0.5	75 cc. 63% EtOH, Δ0.5 h.	Ethane, 90	....
		Dibenzoylmethoxyethylene		
Zn + AcOH	2.0	Zn + AcOH, A	Furan, 75	Ethane,[d] 2, + oil[e,f]
	0 5	0 5 cc. AcOH, 25 cc. 95% EtOH, Δ1 h.	Furan, 32 + oil[c]	....
$Na_2S_2O_4$	2.0	20 cc. 75% EtOH, A25 min.	Furan, SO + oil[e]	Oil[e]
	2 0	32 cc. 60% EtOH, A40 min.	Methoxyethane, 75: furan, 2	....
$CrCl_2$ (EtOH)	2 0	In Δ95% EtOH, add $CrCl_2$	Furan, 23%, + oil[e]	Ethane[d] (tr.) + oil[c]
	6 0	In 80 cc. cold 50% EtOH, add $CrCl_2$, then A	Methoxyethane, 40; ethane,[d] 5	....
		Di-(4-chlorobenzoyl)-methoxy-ethylene		
Zn + AcOH	2 0	14 cc. AcOH, 1 cc. Ac_2O, A	Furan, 55	Recov. 40; ethane,[d] 10; furan, 4
	2.0	In 50 cc. AcOH at 70°, add Zn	Furan, 31; methoxyethane, 43; mixture, 10	Recov. 77; ethane 13; furan, 1.5
$Na_2S_2O_4$	6.0	150 cc. 76% EtOH, Δ20 min.	Methoxyethane, 95	Recov.
	2.0	100 cc. 95% EtOH, A1 h.	Furan, 53	....
		Di-(4-bromobenzoyl)-methoxy-ethylene		
Zn + AcOH	1 0	6 cc. AcOH, A	Furan, 82	Recov. 25; ethane[d,g] 20; furan, 16
		AcOH, EtOH (equal vol.), 3.	Largely furan	Recov. 61; ethane,[d] 6
	2.0	In AcOH at 70°, add Zn	Furan, 54; methoxyethane. 25	....
$Na_2S_2O_4$	6.0	150 cc. 76% EtOH, A 20 min.	Methoxyethane, 75	Recov. 96
	3.0	150 cc. 95% EtOH, Δ1 h.	Recov. 34; furan, 26; methoxyethane, 73	Recov. 95
$CrCl_2$ (EtOH)		Cold 9570 EtOH	Methoxyethane, furan (trace)	....
	2.0	In 50 cc. Δ95% EtOH, add $CrCl_2$	Methoxyethane, 53; furan, 43	....
		Dibenzoylphenoxyethylene		
Zn + AcOH	3 0	75 cc. AcOH, 25 cc. Ac_2O, A, add Zn	Phenoxyethane,[h] 60; furan, 37	Recov. 94
		Dibenzoyl-(4-methylphenoxy)-ethylene		
Zn + AcOH	2 0	85 cc. AcOH, 25 cc. Ac_2O, A, add Zn	Aroxyethane,[i] 43; furan, 24	Recov. 91

[a] The symbol "A" indicates heating the solution to boiling or heating at the boiling point (unless another temperature is specified).

[b] "Recov." = starting material recovered unchanged.

[c] When the amount of reducing agent is not specified a considerable excess was used. Reagents were added in the order named.

[d] "Ethane" refers to the saturated 1,4-diketones from which the niethoxyl or aroxyl group has been eliminated.

[e] The dibenzoylmethoxyethanes were often obtained as oils and in these cases no attempt was made to crystallize them. When dissolved in methyl alcohol and cooled, no crystalline products were isolated (other than those specified). Even small amounts of the furans crystallized from mixtures under these conditions. These residual oils are therefore assumed to consist largely of dibenzoylmethoxyethane.

[f] If the furan is not mentioned it was not found among the products.

[g] A sample of this ethane was prepared by reduction of the dl- and *meso*-di-(bromobenzoyl)-dibromo-ethanes by means of zinc and acetic acid, both isomers yielding the same di-(bromobenzoyl)-ethane (known), Hale and Thorpe, THIS JOURNAL, 35, 272 (1913).

[h] The crude diphenylphenoxyfuran was freed from the last traces of the less soluble dibenzoylphenoxyethane by dissolving in hot alcohol and allowing to cool quietly to room temperature. The furan separated first and was filtered off rapidly; the ethane, remaining up to this point in supersaturated solution, immediately crystallized from the filtrate.

[i] The separation of the 4-methylphenoxy derivatives was facilitated by the following procedure. A hot alcohol solution of the mixture was allowed to cool quietly to room temperature and was seeded with the ethane. Bunches of radiating hair-like needles spread rapidly through the solution, and were quickly filtered off. The furan, remaining up to this point in supersaturated solution, rapidly crystallized from the filtrate and was obtained nearly pure.

The reductions with sodium hydrosulfite were carried out in alcohol as the solvent, but varying amounts of water were added in order to increase the solubility of the reducing agent and to decrease the dehydrating action of the solvent. The procedure was the same in every case. The substance being reduced was placed in a mixture of alcohol and water, sodium hydrosulfite was added and the mixture was boiled under a reflux condenser. The products were isolated by diluting the mixture with water, allowing the gummy precipitate to settle out (usually overnight) and then fractionally crystallizing the residue in order to isolate the components; products in every case were identified finally by mixed melting points with known materials. The yields in Table II refer to nearly pure products actually separated out, and which melted within a few degrees of the theoretical.

Reductions with zinc and acetic acid were carried out by heating a mixture of the substance and the reducing agent under the conditions selected, followed by rapid suction filtration while hot to remove the zinc. The filtrate was diluted with water and allowed to stand (usually overnight) until the gummy precipitate settled. The residue was separated by fractional crystallization (usually from alcohol) into its components, which were identified in every case by mixed melting point methods.

Chromous chloride reductions were carried out in alcohol as the solvent. The reagent was prepared by treating 50 g. of chromic chloride with 350 cc. of alcohol, 50 g. of zinc and 100 cc. of concd. hydrochloric acid. It was preserved under an atmosphere of hydrogen in a suitable apparatus.

Reductions were carried out in closed vessels protected by an atmosphere of carbon dioxide. In a few experiments the reducing agent was introduced through the side arm of the reaction flask into a rapidly boiling solution of the substance to be reduced, the chromous chloride being protected from the air by the vapor of the solvent. The products were isolated by diluting with water, fractionally crystallizing the gummy precipitate from some solvent (usually methyl or ethyl alcohol) and identifying the products in the usual way by means of mixed melting points.

The Action of Reducing Agents on Saturated 1,4-Diketones.—Samples of the saturated 1,4-diketones were tested with the reducing agents under conditions identical with those under which the reductions of the unsaturated 1,4-diketones were carried out. Although smaller amounts of materials were used, the same proportions were maintained. In these experiments the oxidized form of the reducing agent was added in order to make sure that conditions were identical with those actually involved during a reduction. Thus sodium bisulfite was added in tests with sodium hydrosulfite as the reducing agent, zinc acetate in zinc and acetic acid reductions and chromic chloride (by rapid oxidation of the chromous chloride through contact with the air) in tests with chromous chloride. The products were isolated and identified in the usual way.

The results of reductions of the six unsaturated 1,4-diketones and the effects of the reducing agents on the saturated 1,4-diketones are given in Table II.

Reduction of 1-Benzoyl-2-trimethylacetylstyrene.—Benzoyltrimethylacetylstyrene was reduced nearly quantitatively under various conditions with zinc, acetic acid and acetic anhydride to the known benzoyl-(trimethylacetyl)-phenylethane (desylpinacoline).[19] This product was found to be unstable when heated with hydriodic acid (sp. gr. 1.96).

Elimination of Methoxyl and Aroxyl Groups by Reduction.—In a number of experiments small amounts of unsubstituted saturated 1,4-

TABLE III[a]

THE ELIMINATION OF METHOXYL AND AROXYL GROUPS FROM SUBSTITUTED SATURATED 1,4-DIKETONES BY THE ACTION OF REDUCING AGENTS

Substituted ethane	Reducing agent	Yield of ethane, %
Dibenzoylmethoxy-	(a) $CrCl_2$, 50% EtOH, cold, then A	5
	(b) 95% EtOH, Zn + AcOH, Δ·	2.
	(c) Add $CrCl_2$ to Δ95% EtOH	Trace
Di-(chlorobenzoyl)-methoxy-	Zn + AcOH, (a) boil, (b) Δ at 70°	10–13
Di-(bromobenzoyl)-methoxy-	Zn + AcOH, Δ to boiling	20
	Zn + AcOH + EtOH, boiled	8–10
Dibenzoyl-(3-methylphenoxy)-	Zn + AcOH, Δ to boiling	Trace

[a] Data drawn from Table II.

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[19] Boon, J. *Chem. Soc.*, 97, 1258 (1910).

diketones were obtained, resulting from the elimination of the methoxyl or aroxyl group through the action of the reducing agents. The loss of methoxyl or aroxyl occurs only in experiments in which the methoxy- or aroxyethanes, $ArCOCH_2CH(OCH_3)COAr$, are the starting materials or are the principal products in the reactions concerned. Apparently these substances do not decompose (splitting out alcohol or phenol) under the most drastic conditions involved during a reduction, namely, boiling in an acetic acid–anhydride mixture. The reaction, therefore, must involve direct reduction. In Table III are listed the methoxy- and aroxyethanes reduced in this manner.

Summary

1. A variety of reducing conditions are described under which six different substituted unsaturated 1,4-diketones are converted into the corresponding furans, and under which conditions the corresponding saturated 1,4-diketones are stable.

2. The bearing of these facts on the theory of 1,6-addition of hydrogen to unsaturated 1,4-dicarbonyl compounds is discussed and the conclusion is drawn that the dienol postulated by the theory is actually formed as the primary intermediate in reduction and accounts for the formation of the furans.

3. The diaryl-methoxy- and aroxy-substituted 1,4-diketones are easily dehydrated to the corresponding furans and decompose on heating into the corresponding dibenzoylethylene and alcohol or phenol.

4. The methoxyl groups in certain cases are eliminated by reduction from the methoxy-saturated 1,4-diketones.

5. New aroxy- and methoxydibenzoylethylenes are described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

ISOMERS OF 2-PENTENE. I. PENTENE-2 FROM 3-BROMOPENTANE AND FROM 3-PENTANOL[1]

BY MARY L. SHERRILL, BELLE OTTO AND LUCY W. PICKETT

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The present study is one of a series involved in an investigation of the preparation and properties of the isomeric 2-pentenes.[2] Wurtz[3] was the first to report the preparation of 2-pentene and the reaction of this with

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[1] Presented in abstract before the Organic Division, at the Swampscott Meeting of the American Chemical Society, September, 1928.

[2] The work originated in the request of Professor Morris Kharasch (September, 1926) that Professor Carr make, in this Laboratory, absorption spectra measurements of a 2-pentene obtained from 3-bromopentane and of an isomeric form of this 2-pentene which Professor Kharasch had obtained by heating 2-pentene in xylene.

[3] Wurtz, *Ann.*, 125, 114 (1863).

hydrogen bromide. Wagner and Saytzeff[4] prepared the 2-pentene from 3-iodopentane and reported an addition of hydrogen iodide to the pentene to form 2-iodopentane. Brochet[5] also reported the formation of 2-iodopentane by this addition reaction. Van Risseghem[6] prepared 2-pentene by the dehydration of 3-pentanol with *p*-toluenesulfonic acid. In the study of the reactions of the double bond Brunel[7] and Cuy[8] used the work of Wagner and Saytzeff to support their theories. Cuy interpreted the addition reactions in support of the theory of alternate polarity in carbon chains. Lucas and collaborators[9] in a series of investigations presented experimental evidence at variance with this theory and advanced in its place the theory of electronic displacement. According to the alternate polarity theory, addition of hydrogen bromide to 2-pentene should give largely 2-bromopentane, but according to the theory of electronic displacement as interpreted by Lucas, the chief product should be 3-bromopentane. In view of the fact that the accuracy of the older work seemed in doubt, Lucas and Moyse[9b] prepared 3-bromopentane and from this the 2-pentene was obtained by the action of alcoholic potash. The 2-pentene was distilled directly into xylene and from the dried xylene solution 2-pentene (boiling between 35 and 37°) was distilled into glacial acetic acid containing hydrogen bromide. The bromide obtained had a refractive index of n_D^{20} 1.4437 and was 78% 3-bromopentane and 22% 2-bromopentane. This percentage was determined entirely by the index of refraction, since Lucas had shown that the refractive index of a mixture of 3-bromopentane and of 2-bromopentane was a linear function of the composition. Lucas considered the electron displacement theory confirmed by these data. Kharasch[10] has determined the relative electronegativity of certain organic radicals and found that the methyl group is more electronegative than the ethyl group. This is in accord with Lucas' ideas but Kharasch disagrees with Lucas as to the resultant condition of the carbons at the double bonds. Lucas and Moyse[9b] state that "methyl exerts a stronger pull on electrons than ethyl does, as shown by the relative ionization constants of organic acids and bases, and therefore 2-pentene, where a methyl and an ethyl radical are situated on opposite sides of the double bond, should have the electrons of this bond closer to the methyl. Therefore when hydrogen bromide adds, the bromine should go largely to the

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[4] Wagner and Saytzeff, *Ann.*, 179, 321 (1875).

[5] Brochet, *Bull. soc. chim.*, [3] 7, 567 (1892).

[6] Van Risseghem, *Bull. soc. chim. Belg.*, 28, 53, 187, 288 (1914).

[7] Brunel and Probeck, *Am. Chem. J.*, 44, 431 (1910).

[8] Cuy, THIS JOURNAL, 42, 503 (1920).

[9] (a) Lucas and Jameson, *ibid.*, 46, 2475 (1924); (b) Lucas and Moyse, *ibid.*, 47, 1459 (1925); (c) Lucas, Simpson and Carter, *ibid.*, 47, 1462 (1925).

[10] Kharasch and Reinmuth, *J. Chem. Ed.*, 5, 404 (1928); Kharasch and Marker, THIS JOURNAL, 48, 3130 (1926).

middle carbon atom." According to the Kharasch theory the substitution of an electronegative atom or radical for a hydrogen in the methyl group decreases the electronegativity of the group, and since the methyl group is more electronegative than the ethyl group, the carbon atom in the ethylenic linkage which carries the methyl group will be *less* electronegative than that which has the ethyl group. As a consequence the pair of electrons should be displaced toward the carbon atom to which the ethyl group is attached and when hydrogen bromide is added to 2-pentene the product should be 2-bromopentane and not 3-bromopentane as would follow from the hypothesis of Lucas.

As a corollary of this theory of the partial polarity of the ethylene bond, Kharasch[11] predicted the existence of electronic isomers in cases where the radicals attached to the two carbon atoms of the double bond differ very slightly in electronegativity, as is the case in 2-pentene. In one isomer the second pair of electrons would be displaced toward the carbon atom to which the ethyl group is attached and in the other isomer toward the carbon atom carrying the methyl group, but the latter isomer should be the less stable. In the preparation of 2-pentene from *3-bromopentane* it was reasonable to expect the formation of the less stable isomer since the carbon atom to which the bromine is attached would have its electronegativity decreased and the electrons would be displaced in such a way that with the splitting off of hydrobromic acid in the formation of the pentene the second pair of electrons of the double bond would be displaced toward the methyl group. This form of 2-pentene should add hydrogen bromide to give 3-bromopentane. Kharasch further postulated the possibility of transforming this form of 2-pentene into the more stable form which should add hydrogen bromide to form 2-bromopentane.

In order to confirm this theory, Kharasch repeated the work of Lucas and, under similar conditions, obtained results identical with those of Lucas. Kharasch found, however, that whereas this 2-pentene, made from 3-bromopentane, in glacial acetic acid added hydrogen bromide to form 78% of 3-bromopentane and 22% of 2-bromopentane, in a non-polar solvent such as carbon tetrachloride or petroleum ether or by direct addition of hydrogen bromide without a solvent, the 2-pentene gave 97–100% of 3-bromopentane. Kharasch then heated a solution of 2-pentene in xylene in a sealed glass tube at 90–100° for varying lengths of time and found that the 2-pentene was gradually transformed into an isomeric form of 2-pentene which gave addition products with hydrogen bromide varying from 63% of 3-bromo- and 37% of 2-bromopentane to 16% of 3-bromo- and 84% of 2-bromopentane depending on the length of time

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[11] Private communication, September, 1926; paper presented at Organic Symposium, Columbus, Ohio, December, 1927. Since the preparation of this article a full discussion of Kharasch's theory has been published in *Chemical Reviews*, 5, 571 (1928).

it had been heated. The percentage composition was determined by the index of refraction of the bromide obtained. This work of Kharasch gave evidence of the two electromers which he had believed theoretically possible. To obtain additional data Professor Kharasch asked Professor Carr to make absorption spectra measurements of these compounds. The preparation, the purification of the 2-pentene and its transformation into the isomeric form were undertaken in this Laboratory, the products to be used for absorption measurements. The addition products and the physical properties of the 2-pentene have been studied. The work of Kharasch has been duplicated and additional data have been obtained.

In view of the fact that for absorption measurements it is highly important to have materials of a high degree of purity, it seemed essential to have the measurements made on each of the pure isomers rather than on possible mixtures. This involved the consideration of methods of separation. In addition to the electronic isomers considered by Kharasch, there is also the possibility, in 2-pentene, of *cis-trans* isomerism. In the present work this possibility has been kept constantly in mind. Van Risseghem[6] attempted the separation of the *cis-trans* isomers of 2-pentene. She prepared the 2-pentene by the dehydrating action of *p*-toluenesulfonic acid on diethylcarbinol at 135–140°. Repeated fractionation through a Young column gave no evidence of separation and since attempts to isomerize also failed she concluded that only one form was stable or that there was an equilibrium mixture of the two. In spite of these results it was considered advisable to use the method so successfully used by Van de Walle[12] in the separation of *cis-trans* isomers of the halogen ethylenes, that is, the fractionation of azeotropic mixtures of the pentenes with absolute alcohol. In the separation of *cis-trans* isomers the alcohol has seemed to have a stabilizing effect and by its use isomers have been separated which had not been separated by any other method. The method has proved highly satisfactory for the purification of the pentenes.

Experimental

Preparation of 3-Pentanol (Diethylcarbinol).—3-Pentanol was prepared by a Grignard synthesis from ethylmagnesium bromide and ethyl formate. A detailed description of the method is given by Lucas and Moyse[9b] and their work was repeated in this Laboratory. The ethyl formate, prepared from ethyl alcohol (6 moles), concentrated sulfuric acid (6.8 moles) and sodium formate (6 moles) was obtained in 90% yield (b. p. 54.2 ± 0.1°). The final distillation of the 3-pentanol gave a product (70% yield) which boiled at 114.8–115.2° and had a refractive index, n^{20}_{D} 1.4078. Lucas and Moyse[9b] give the boiling point as 117–119° (corr.) at 745 mm. The values given by other investigators[13] correspond more closely to that obtained in this Laboratory.

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[12] Van de Walle, Bull. *soc. chim. Belg.*, 27, 209 (1913); *Mémoires de l'Acad. roy. Belg. Classe des Sciences,* 2e serie, 7, 49 (1923); Bull. *soc. chim. Belg.*, 34, 10,339 (1925); 35, 29 (1926).

[13] Timmermans, *ibid.*, 27, 334 (1913), gives 115.35 ± 0.10" at 760 mm.; Willcox

In addition to the 3-pentanol prepared in this Laboratory, pentanol-3 (synthetic) was obtained from R. E. Marker. This material (b. p. 114–116.8° corr., and n_D^{20} 1.4078) was used in some comparison runs. Commercial 3-pentanol (Sharples Solvents Corporation) was fractionated several times through a 50-cm. Crismer column and gave fractions 114–115.8°, n_D^{20} 1.4078, and 115.8–116.2°, n_D^{20} 1.4079. This material was used only in trying some variations of method and not for any of the conclusive experiments.

Preparation of **3-Bromopentane.**—This compound was formed by treating the carbinol according to the method given by Kharasch.[14] The carbinol was placed in a round-bottomed flask and cooled to −10°. It was then saturated with hydrogen bromide which was obtained by the action of bromine on red phosphorus and water, passed through U-tubes containing moist red phosphorus and one tube containing anhydrous sodium sulfate. After saturation the flask containing the carbinol was closed with a stopper to which a toy rubber balloon was attached and was heated in a water-bath up to 60° and kept at that temperature until the collapse of the balloon indicated complete absorption of the hydrogen bromide. This saturation process was repeated several times until no more gas was absorbed. The product was separated from the hydrobromic acid–water layer, washed four times with ice water, twice with ice-cold concentrated sulfuric acid, once with ice water, twice with a cold saturated solution of sodium carbonate and once with ice water. It was then dried over potassium carbonate and distilled from a flask with fractionating neck. The 3-bromopentane was obtained in 84–85% yields and had the following properties: boiling point, 118.2–118.5" at 760 mm.; n_D^{20} 1.4443 (Abbé), 1.44431 (Zeiss dipping); d_4^{20} 1.2170. Repetition of the above procedure in many runs gave identical results. The process was slow and in an effort to hasten the process variations in the above procedure were tried which brought out the interesting fact that unless great care was taken in the preparation of the bromopentane the product was not pure 3-bromopentane but a mixture of 3-bromopentane and 2-bromopentane (b. p. 117.5–118.5° at 745 mm., n_D^{20} 1.4415).[9c,3] The variations in treatment of the carbinol were the use of gaseous hydrogen bromide under pressure,[9b] the action of phosphorus tribromide in the cold and gently warmed

TABLE I

RESULTS OF EXPERIMENTS

		B. p. at 760 mm., °C.	n_D^{20}
A. By saturation with gaseous hydrogen bromide at −10° and warming to 60°			
(1) Atmospheric pressure (repeated runs)		118.2–118.5	1.44431
(2) Increased pressure	(a)	118 –118.5	1.4443
	(b)	117.5–118.3	1.4432
	(c)	117.6–119.1	1.4427
	(d)	36 at 43 mm.	1.4422
B. By action of phosphorus tribromide			
	(a)	116.5–118.5	1.4424
	(b)	115 –118.5	1.4404
C. By action of 48% hydrobromic acid			
	(a)	115–118	1.4419
	(b)	115–118	1.4422

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and Brunel, THIS JOURNAL, 38, 1838 (1916), give 114.8–115.2° at 760 mm.; Brunel, *ibid.*, 45, 1337 (1923), gives 115.4" at 754 mm., n_D^{25} 1.4077; Norris and Cortese, *ibid.*, 49, 2644 (1927), give 115.8–116° and n_D^{25} 1.4079.

[14] Kharasch, private communication, 1926.

to 60° and the action of 48% hydrobromic acid refluxed for several hours. Table I shows the variations in the product obtained.

Not only does the variation in boiling point and refractive index give evidence of the presence of 2-bromopentane in these products, but the absorption spectra of 2-pentene obtained from these give more conclusive evidence of this.[15] The results obtained in C indicated the probable course of the transformation. In that case a considerable amount of 2-pentene distilled over. The hydrocarbon is therefore evidently formed by the more vigorous method and after being formed under these conditions of higher temperature or pressure adds to form 2-bromopentane in varying amounts. This may be considered as some evidence in favor of the fact that this 2-pentene is the more stable form of 2-pentene.

Preparation of 2-Pentene

A. From 3-Bromopentane by the Action of Alcoholic Potash.—Bromopentane-3 (n^{20}_D 1.4443, 229 g.) was dropped slowly into a solution of potassium hydroxide (261 g.) in absolute methyl alcohol (500 cc.) heated on an oil-bath kept at 110–115°. The vapors were passed through a reflux condenser kept at 40°, then through a cold downward condenser and the distillate was collected in absolute methyl alcohol protected from the moisture of the air and kept cold with ice and salt. When ethyl alcohol was used as the collecting solvent it was then used for the alcoholic potash and the temperature of the bath was 125–127°. The distillate was fractionated through a Crismer column (50 cm. or 1.5 m. in various runs) surrounded by an air jacket and the azeotropic mixture which was distilled was collected in a flask surrounded by ice and salt. The 2-pentene was separated from the alcoholic solution by repeated washings with ice water; then it was dried over calcium chloride. The yield of 2-pentene was 89–92%. Whenever pure 3-bromopentane (n^{20}_D 1.4443) was used the distillation of the azeotropic mixture was practically constant throughout, and the 2-pentene isolated was pure. When, however, the 3-bromopentane used contained some 2-bromopentane, the distillation was not constant, and the hydrocarbon isolated had different physical properties. This variation is shown in Table II.

TABLE II

RESULTS OF EXPERIMENTS

				2-Pentene	
		n^{20}_D		B. p. at 760 mm., °C.	n^{20}_D
1	3-Bromopentane	1.44431		36.30 ± 0.05	1.37963
2	3-Bromopentane	1.4437	after 2d fractionation		1.37935
			after 3d fractionation		1.37945
3	3-Bromopentane	1.4432			1.37930
4	3-Bromopentane	1.4427			1.37923
5	3-Bromopentane	1.4417			1.3791

The rate of fractionation of azeotropic mixtures of the pure 2-pentene and of a mixture done simultaneously is shown in Fig. 1, Curve I, representing the fractionation of 2-pentene from (1) above, and II representing the fractionation of 2-pentene from (4) above.

B. From 3-Pentanol by the Action of 60% Sulfuric Acid.—The method is that reported by Norris,[16] in which commercial 2-pentanol was treated with sulfuric acid.

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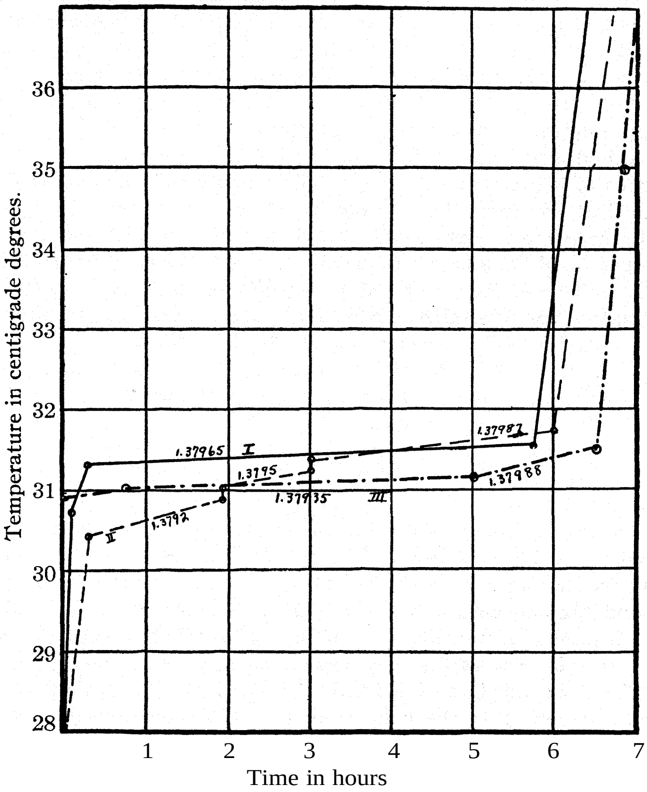
[15] Carr, THIS JOURNAL, 51, 3041 (1929).

[16] (a) Norris and Reuter, *ibid.*, 49, 2630 (1927); (b) Norris and Joubert, *ibid.*, 49, 885 (1927), had dehydrated 3-pentanol with phosphorus pentoxide.

A 60% solution of sulfuric acid (containing 105 g. of concentrated acid) was placed in a flask provided with a drop funnel and connected with a long condenser, and 3-pentanol (43 g.) was slowly added from the funnel. The flask was cooled in ice and shaken gently during the addition of the alcohol. The mixture was then heated slowly on a water-bath and finally on a boiling water-bath as long as the hydrocarbon distilled. The distillate was collected in a bottle surrounded by ice and salt. It was washed with 5% sodium hydroxide and dried over calcium chloride; yields, 73-90%. The crude pentene had a refractive index of 1.3820–1.3823 at 20". Refractionated as an azeotropic mixture with methyl alcohol the following fractions were obtained.



——, I, 2-Pentene from 3-bromopentane, n^{20}_{D} 1.44431 (762 mm.); – –, II, 2-pentene from 3-bromopentane, n^{20}_{D} 1.4427 (762 mm.); — - —, III, 2-pentene from 3-pentanol, n^{20}_{D} 1.4078 (755 mm.).

Fig. 1.—Fractionation of azeotropic mixtures of 2-pentane in methyl alcohol.

	B. p. at 760 mm.., °C.	Time	Wt. of 2-pentene, g.	n^{20}_{D}
I	31.1–31.2	45 min.	6.7	1.3793
II	31.2–31.3	4 hours	11.7	1.3794
III	31.3–31.7	1.5 hours	12.9	1.37988

Fractions I and II, from absorption spectra measurements, were identical and when mixed gave a refractive index of 1.37935 at 20°. The lower index and lower boiling azeotropic mixture would indicate a small amount of the isomeric 2-pentene. Fraction III contained a large amount of more absorptive material, the higher index being due to this. This may be polymeric material and it is present in much greater quantities in 2-pentene made by this method than in that from the alcoholic potash method. The alcoholic solution after fractionation was washed with water and gave a large amount of a residue of high index, much larger than any ever obtained by the other method.

In addition to the method given for the preparation of 2-pentene, the dehydration of the 3-pentanol by *p*-toluenesulfonic acid was tried. The product obtained, however, contained an impurity which was very absorptive in the ultraviolet and therefore made the method of no value for the purposes of this problem.

Properties of 2-Pentene.—The azeotropic mixture with methyl alcohol boiled at 31.40 ± 0.05' at 760 mm. Fifty grams of the mixture gave 47 g. of the 2-pentene (87%). The azeotropic mixture with ethyl alcohol boiled at 34.7 ± 0.05". The physical properties of the 2-pentene were obtained as follows and comparative literature data are also given. Boiling point, 36.40 ± 0.05°, 760 mm.; d_4^{20} 0.6503; n_D^{20} 1.37965 (Zeiss dipping); Van Risseghem,[6] b. p. 36.40°, 760 mm.; d_4^{11} 0.6595; n_D^{11} 1.3857; $d_4^{17.2}$ 0.6535; $n_D^{17.2}$ 1.3817. Auwers,[17] b. p. 36–37°; d_4^{20} 0.653; n_D^{20} 1.3812. Lucas and Moyse,[9b] b. p. 35–36°. Norris and Joubert,[16b] from synthetic 3-pentanol, b. p. 36–37.5°. Norris and Reuter,[16a] from 2-pentanol (commercial), b. p. 36.39 ± 0.04°, 760 mm.; d_4^{20} 0.65054; n_D^{20} 1.38081.

Addition Reactions of 2-Pentene.—Since Lucas and Moyse[9b] used the addition reaction of hydrogen bromide to 2-pentene as conclusive proof of their theory and since the directive addition of an unsymmetrical substance as hydrogen bromide should in the case of electronic isomers give different products, it was necessary to study the addition under varying conditions. The possible addition products formed by the action of hydrogen bromide on 2-pentene are 3-bromopentane (b. p. 118.2–118.5°, n_D^{20} 1.4443) and 2-bromopentane (b. p. 117.5–118.5°, n_D^{20} 1.4416). Lucas and co-workers[g]" have shown that the refractive index of mixtures of the two bromides is a linear function of the composition. The addition of bromine to 2-pentene should give 2,3-dibromopentane. The dibromide formed had b. p. 178–179°, n_D^{33} 1.5010, n_D^{20} 1.5074, n_D^{15} 1.5102. Wagner and Saytzeff[4] gave the boiling point as 178° uncorrected. Van Risseghem[6] gives the boiling point as 60.5–61° at 14 mm.; n_D^{17} 1.50926; n_D^{11} 1.5119. Norris and Reuter[16a] prepared the dibromide by addition of bromine to 2-pentene (36.3–36.4°) made from 2-pentanol and obtained a dibromide which boiled with slight decomposition at 180.2–180.8" at 754 mm. and had a refractive index, n_D^{20} 1.5098; n_D^{10} 1.5149. These values are higher than other recorded values ("International Critical Tables," b. p. 175°, n_D^{15} 1.5094) and higher than those obtained in this Laboratory (given previously). The fact that the Ppentene used by Norris and Reuter may have had some 1-pentene in it may account for the higher values. The 1,2-dibromide boils at 184° corr. at 760 mm. and 68° at 12 mm. and the refractive index is n_D^{21} 1.5088 according to Kirrmann.[18]

Reaction of 2-Pentene with Hydrogen Bromide.—The 2-pentene, either pure or in a solvent, was placed in a flask surrounded by ice and salt mixture and saturated with gaseous hydrogen bromide. The hydrogen bromide was prepared as given above, in the preparation of 3-bromopentane, but an additional tube containing naphthalene (to remove traces of bromine) was added to the drying train. The saturation was repeated two or three times, then the bromopentane was washed in the usual way with

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[17] Auwers, *Ann.*, 415, 142 (1916).

[18] Kirrmann, *Bull. soc. chim.*, [4] 39, 989 (1926).

ice water, ice-cold sulfuric acid, with water, sodium carbonate Qnd water. The dried products were distilled in fractionating flasks and the refractive indices taken. When the addition reaction was carried out in a non-polar solvent such as carbon tetrachlaride or with the 2-pentene without a solvent, the product was almost pure 3-bromopentane. When the solvent was a polar one, as glacial acetic acid, the product was 78% 3-bromopentane and 22% 2-bromopentane, as found by Lucas and Moyse.[9b] When the 2-pentene was prepared from a mixture of 2- and 3-bromopentanes the quantity of 2-bromopentane obtained by addition of hydrogen bromide was considerably greater. It was found also that if the addition of hydrogen bromide was not made very carefully at low temperatures (−10°), a larger proportion of 2-bromopentane was formed. The 2-pentene made from mixtures of 3-bromopentane and 2-bromopentane might also contain some 1-pentene and the resultant bromopentane might then contain some 1-bromopentane (n_D^{20} 1.4444, I. C. T.). Representative data are given in Table III.

Reaction of 2-Pentene with Bromine.—The 2-pentene, dissolved either in glacial acetic acid or carbon tetrachloride, was cooled in ice and salt and *a* solution of bromine in the corresponding solvent was added drop by drop until a permanent yellow color remained. The amount absorbed was in every case practically the theoretical quantity. The dibromide was washed and dried in the same way as the monobromide. Whenever pure 2-pentene was used, there was only one product, the 2,3-dibromide, formed as indicated by the distillation temperature and the refractive index. In some cases where the 2-pentene used had been made from a mixture of 3-bromopentane and 2-bromopentane and therefore might possibly have had a small amount of 1-pentene present, there was a small amount of higher-boiling dibromide, probably the 1,2-dibromide. Some representative data are given in Table III.

TABLE III

REPRESENTATIVE DATA

Bromopentane from which 2-pentene was prepared, n_D^{20}	Pentene, n_D^{20}	Addn. prod. with HBr B. p. (760 mm.), °C.	Addn. prod. with HBr n_D^{20}	Addn. prod. with Br_2 B. p. (760 mm.), °C.	Addn. prod. with Br_2 n_D^{20}
(1) 1.44431	1.37965	118–118.5	1.4442 (in CCl_4) (98% 3-bromo)	178–179	1.5074 (100% 2, 3-dibromo)
		118–118.5	1.4437 (in glacial acetic acid) (78% 3-bromo, 22% 2-bromo)		
(2) 1.4437	1.37935 (2d fractionation)	Without solvent	1.4422 12%[a]	178–179	1.5074 85%[a]
			1.4430 75%[a]	179–182	1.5090 15%"
			3.4441 12%[a]		
	3d fractionation		1.4429		
			1.4434		
(3) 1.4432	1.37930		1.4426		
(4) 1.4427	1.37923		1.4430		
(5) 1.4417	1.3791	117–118	1.4429		
		118–121	1.4434		
Pentanol from which 2-pentene was prepared					
1.4079	1.37935		1.4434 (in glacial acetic acid) (66% 3-bromo, 34% 2-bromo)		

[a] The percentages in (2) above are based on the weights of the fractions obtained.

Transformation of 2-Pentene into an Isomeric Form.—Kharasch[14] had found that the 2-pentene prepared from 3-bromopentane when heated in xylene gave an isomeric form. In the work in this Laboratory it was found that heat alone did not produce this change but that light was necessary. Since, too, the presence of even a minute trace of xylene was detrimental to absorption spectra measurements, the use of this solvent was avoided and the 2-pentene, without any solvent, was exposed to sunlight and ultraviolet light.

(1) Some of the 2-pentene (n_D^{20} 1.37965) was sealed in a glass tube and heated in a water jacket at 70–SO° at intervals for a total of sixty-five hours and was then left in the laboratory under a skylight for thirteen weeks, thus exposed to the available sunlight. At the end of this time, the tube was opened and the material investigated. The refractive index was taken, the absorption spectra were measured and addition compounds with hydrogen bromide and with bromine were prepared. The data are given in Table IV.

(2) Some 2-pentene (n_D^{20} 1.37945) from the third fractionation of 2-pentene from bromopentane (n_D^{20} 1.4437) was placed in a small quartz flask fitted with a reflux condenser; the flask and condenser were kept cold with solid carbon dioxide and the flask was placed about 10–12 cm. away from an Hanovia quartz mercury vapor lamp. The material was exposed to the ultraviolet light for a total of four hours and thirty minutes. Absorption spectra measurements were made after one hour and fifty minutes, after three hours and forty minutes and after four hours and thirty minutes. The physical properties were determined and the addition reactions of this transformed 2-pentene were studied. The data are given in Table IV.

(3) Some 2-pentene (n_D^{20} 1.37930) which had been prepared from 3-bromopentane (n_D^{20} 1.4432) containing a little 2-bromopentane as an impurity, was placed in a quartz flask with a reflux condenser, cooled with solid carbon dioxide and exposed to ultraviolet light for eight hours and thirty minutes. The data obtained from the transformed material are given in Table IV. Some of the transformed material was fractionated with methyl alcohol and three fractions were obtained. The boiling point of each of these mixtures was lower than the boiling point of the azeotropic mixture of the original untransformed material, indicative of a transformation to the lower-boiling form.

		Azeotropic mixture, b. p. at 760 mm., °C.	Refractive index of the pentene, n_D^{20}
Original material		31.3 –31.4	1.37930
Material after transformation	(1)	30.5 –30.9	1.3793
	(2)	30.95–31.15	1.3792
	(3)	31.15–31.25	1.3795

The bromide formed from the third fraction had a somewhat higher index and higher boiling point than the bromide made from the unfractionated sample of the transformed material, showing that the two isomers were partially separated.

The following points are worthy of note: (1) the azeotropic mixture of the transformed material has a lower boiling point and a wider range than the original; this seems indicative of a mixture. (2) The transformed pentene boils over a wider range than the untransformed. (3) The refractive indices of the transformed material are lower than those of the original except in the case of long exposure to ultraviolet light, and

TABLE IV

DATA OF TRANSFORMED MATERIAL

			Transformation product		
		Untransformed 2-pentene	(1) Sunlight	(2) Ultraviolet 4.5 hrs.	(3) Ultraviolet 8.5 hrs.
1	B. p. of azeotropic mixt. with MeOH	31.35 ± 0.05°	.....	.....	30.50–31.25°
2	B. p. of 2-pentene	36.30 ± 0.05°	.....	.....	36.4 ± 0.20°
3	n^{20}_D	1.37965	1.37934	1.37937	1.37956
4	d^{20}_4	0.6503	......	0.6500	.....
5	n^{20}_D of monobromide	1.4437 (78% 3-bromo, 22% 2-bromo)	1.4420 (15% 3-bromo, 85% 2-bromo)	1.4423	1.4421 (av.)
6	n^{20}_D of dibromide	1.5074	1.5074	.....	.....

the increase here may be due to the formation of polymeric material or decomposition products. There is evidence of this in the absorption measurements. (4) The monobromide from the transformed material is largely 2-bromopentane rather than 3-bromopentane, as in the case of the untransformed 2-pentene. (5) The dibromide formed from the light-transformed pentene is identical with that from the original pentene, indicating that there has been no shift in the double bond. There was a possibility of a racemic mixture or a *meso* form if isomers were *cis-trans*, but no evidence of two kinds has been obtained.

Summary

1. Pentene-2 has been prepared from 3-bromopentane and from 3-pentanol. This has been purified by fractionation of constant-boiling mixtures with methyl and with ethyl alcohol. The physical properties of this 2-pentene have been determined. This pentene adds hydrogen bromide in a non-polar solvent such as carbon tetrachloride to give 98–99% of 3-bromopentane. In glacial acetic acid it adds hydrogen bromide to give 78% of 3-bromopentane and 22% of 2-bromopentane. Addition of bromine to this 2-pentene gives 2,3-dibromopentane.

2. Sunlight and ultraviolet light transform this 2-pentene into an isomeric form which has slightly different physical properties. The transformed 2-pentene adds hydrogen bromide to form 15% of 3-bromopentane and 85% of 2-bromopentane. With bromine it forms the same dibromopentane, 2,3-dibromo-, as the original 2-pentene.

3. The 3-bromopentane can be prepared pure only by great care in the hydrobromination of the 3-pentanol. Strong reagents like phosphorus tribromide or higher temperatures and pressures give mixtures of 3-bromopentane and 2-bromopentane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

ISOMERS OF 2-PENTENE. II. PENTENE-2 FROM 2-BROMOPENTANE AND FROM 2-PENTANOL[1]

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The transformation of 2-pentene prepared from 3-bromopentane by the action of ultraviolet light or by diffused light into an isomeric form differing slightly in physical properties and radically in the addition product formed by hydrogen bromide was indicative of electronic isomerism.[2] If these were electronic isomers then it ought to be possible to use as initial material 2-bromopentane in which the strongly electronegative bromine atom was attached to the second carbon atom (C-2) making it less electronegative than the adjacent carbon (C-3) and to obtain a 2-pentene in which the carbon atom (C-3) of the double bond adjacent to the ethyl group would be more electronegative than the carbon atom (C-2) adjacent to the methyl group. This 2-pentene should be the stable form and should be identical with the product obtained by the action of light on the 2-pentene obtained from 3-bromopentane. Lucas, Simpson and Carter[3] had prepared 2-pentene from 2-bromopentane but made no effort to separate it from the 1-pentene formed at the same time nor to compare it in physical properties with the 2-pentene from 3-bromopentane. The addition of hydrogen bromide to the mixture of 1-pentene and 2-pentene was carried out and the product obtained was fractionated but in view of the fact that the refractive indices of 1-bromopentane (n_D^{20} 1.4444, "I. C. T.") and of 3-bromopentane (n_D^{20} 1.44431) are so nearly identical and the boiling points of 2-bromopentane (117.5–118°) and of 3-bromopentane (118.2–118.5°) are so close together, the inferences made from the data are not conclusive.

The chief difficulty in the preparation of 2-pentene from 2-bromopentane or 2-pentanol lay in the fact that the removal of hydrogen bromide or the dehydration of 2-pentanol gave as products both 2-pentene and 1-pentene and a complete separation of these was necessary. Lucas, Simpson and Carter[3] estimated that from 2-bromopentane approximately 71% of 2-pentene and 29% of 1-pentene was obtained. Norris and Reuter[4] prepared 2-pentene by the dehydration of secondary amyl alcohol manufactured from petroleum and obtained a 90% yield of the hydrocarbon boiling between 36.5 and 40°. The amount of 1-pentene was not estimated. The data found in the literature with regard to 1-pentene are contradictory.

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[1] Presented in abstract before the Organic Division at the Swampscott Meeting of the American Chemical Society, September, 1928.

[2] Sherrill, Otto and Pickett, THIS JOURNAL, 51, 3023 (1929).

[3] Lucas, Simpson and Carter, *ibid.*, 47, 1462 (1925).

[4] Norris and Reuter, *ibid.*, 49, 2630 (1927); *cf.* "Organic Syntheses," Wiley and Sons, New York, 1927, Vol. VII.

Brochet[5] in the fractionation of boghead gas obtained a product, designated 1-pentene, with a boiling point 39–40°. Norris and Joubert[6] prepared 1-pentene from ethylmagnesium bromide and allyl bromide. The product obtained after rather rigorous treatment to remove the halide and the diethyl ether boiled at 39–41'. Some diallyl, boiling at 59–61", was also obtained. Kirrmann[7] had prepared 1-pentene by a similar synthesis but the Grignard reagent was added to the allyl bromide to diminish polymerization and the solvent used was dipropyl ether, which being of much higher boiling point did not have to be removed by vigorous treatment with concentrated hydrochloric acid as in the Norris method. The boiling point of 1-pentene is given by Kirrmann as 30.5–31" at 767 mm. Bourguel[8] has prepared 1-pentene by the hydrogenation of a true acetylene pentine ($CH_3CH_2CH_2C{\equiv}CH$). The boiling point of 1-pentene as given by Bourguel is 32.5" at 760 mm. Bourguel found, in a series of hydrocarbons, that the hydrocarbon with the double bond between the first and second carbon atoms boiled lower than the one with the double bond between the second and third carbon atoms.

The results in the present work depended upon the separation of 1-pentene from 2-pentene and it was believed to be possible by the fractionation of an azeotropic alcohol mixture as used in the purification of the 2-pentene prepared from 3-bromopentane and 3-pentanol.[2] This method has been used with very satisfactory results. 2-Pentene, practically free from 1-pentene, has been obtained and its properties are different from those of the 2-pentene prepared from 3-bromopentane and 3-pentanol but are almost identical with those of the 2-pentene which had been transformed by light.

Experimental

Preparation of **2-Pentanol (Methyl-*n*-propylcarbinol).**—Secondary amyl alcohol was prepared according to the method of Wood and Scarf by the action of *n*-propylmagnesium bromide on acetaldehyde.

Propyl Bromide.—Normal propyl bromide (Eastman Kodak Co.) was purified by washing with concentrated sulfuric acid (ice cold) and with sodium hydroxide (2 M) until neutral, was dried and distilled, the fraction boiling at 71–71.2° being used.

Grignard Synthesis—The Grignard reagent was prepared in the usual way, 75 g. of magnesium (3.1 moles) and 394 g. (3 moles) of n-propyl bromide being used. The reaction mixture was stirred for two hours after all of the propyl bromide had been added. Then the required amount of acetaldehyde was passed into the reaction mixture, which was kept cold in an ice and salt mixture and was stirred continuously. The acetaldehyde was distilled from a flask provided with a reflux condenser; the water through the condenser was kept at 40°. From the condenser a tube led to a

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[5] Brochet, *Bull. soc. chim.*, [3] **7**, 567 (1892).

[6] Norris and Joubert, THIS JOURNAL, **49**, 885 (1927).

[7] Kirrmann, *Bull. soc. chim.*, [4] **39**, 988 (1926).

[8] Bourguel, *ibid.*, [4] **41**, 1476 (1927).

[9] Wood and Scarf, *J. Soc. Chem. Ind.*, **42**, 13T (1923).

combustion tube containing calcium chloride and a tube from this led to the bottom of a side-arm test-tube. The test-tube was connected with a three-way stopcock, one arm of which was attached to a tube leading into the Grignard reaction flask. The aldehyde was heated on a water-bath (30–35°) and dried by passing over calcium chloride. In the beginning the test-tube was chilled so that enough aldehyde was condensed to a liquid, then the rate at which the gas bubbled through this served as a gage for the speed of addition of aldehyde to the reaction flask. After the addition of the aldehyde the reaction mixture was stirred for twelve hours. Then part of the excess ether and the excess aldehyde was distilled from the reaction mixture and the mixture decomposed with ice and ammonium chloride. The 2-pentanol was extracted with ether. The water layer was steam distilled and the distillate also extracted with ether. From the ether extracts 2-pentanol was obtained, boiling at 118.5–119.5° at 760 mm. and having a refractive index n^{20}_{D} 1.4060. The literature data for the methyl-n-propylcarbinol are as follows. Brunel[10] gives the boiling point as 119.275° at 754 mm. and index n^{25}_{D} 1.4043; Norris and Cortese[11] give the boiling point as 119.16–119.26' at 760 mm. and n^{25}_{D} 1.4048. "International Critical Tables" gives secondary amyl alcohol as b. p. 119.5°, 760 mm., and n^{20}_{D} 1.4072 and for d-secondary amyl, b. p. 118° and index n^{20}_{D} 1.4053. The yields of the carbinol were poor, due in part to the formation of hydrocarbons in the reaction and in part to acetal formation. Commercial 2-pentanol (Sharples Solvents Corporation) was fractionally distilled several times through Crismer columns and some very constant boiling fractions, b. p. 118–118.5°, $n^{20°}_{D}$ 1.4073, were obtained. This material was used in some comparison runs.

Preparation **of 2-Bromopentane.—The** 2-pentanol was hydrobrominated by the method given for the preparation of 3-bromopentane,[2] by the saturation of the 2-pentanol with hydrogen bromide at —10' and then by warming the mixture to 60° under atmospheric pressure. The product was purified as in the case of the 3-bromopentane, dried and distilled. The boiling point was 117–118° at 760 mm. and the refractive index was n^{20}_{D} 1.4412. Lucas, Simpson and Carter[3] give the refractive index as n^{20}_{D} 1.4416. In cases where the hydrobromination was carried out under increased

TABLE I

REPRESENTATIVE DATA

A. By saturation with gaseous hydrogen bromide at −10° and warming to 60°

			B. p. at 760 mm.. °C.	n^{20}_{D}
(1)	Atmospheric pressure (repeated runs)		117–118	1.4412
(2)	Increased pressure	(a)	114.5–118	1.4416
		(b)	116.5–118	1.4416
	B. By the action of phosphorus tribromide			
(1)	Cold		116–117.5	1.44123"
(2)	Heated	(a)	116–117.5	1.4419
		(b)	116–118	1.4420
	C. By the action of 48% hydrobromic acid			
		(a)	116.5–118	1.4417
		(b)	117–119	1.4419

[a] The 2-bromopentane B (1) was obtained from R. E. Marker (prepared from synthetic 2-pentanol). It was refractionated in this Laboratory. The index was taken on a Zeiss dipping refractometer.

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[10] Brunel, THIS JOURNAL, 45, 1337 (1923).

[11] Norris and Cortese, *ibid.*, 49, 2644 (1927).

pressure the value obtained in this Laboratory was also n_D^{20} 1.4416. It should be noted that the 2-bromopentane is much more easily obtained as a rather pure compound than is the 3-bromopentane. Table I gives representative data.

Preparation of 2-Pentene

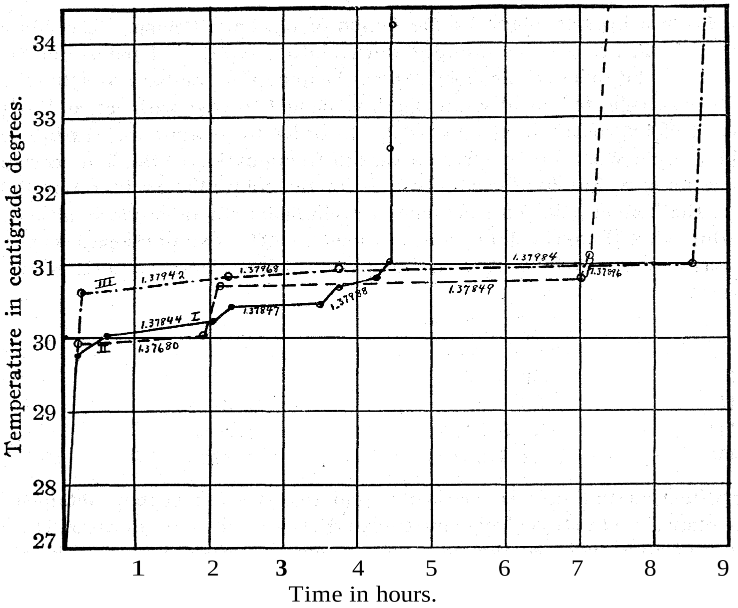
A. From 2-Bromopentane by the Action of Alcoholic Potash.—The 2-bromopentane (n_D^{20} 1.4412, 229 g.) was dropped slowly into a solution of potassium hydroxide (261 g.) in absolute methyl alcohol (500 cc.) heated on an oil-bath at 110–115°. The 2-pentene was collected in absolute methyl alcohol, cooled with ice and salt. The crude yield of hydrocarbon was 85–90%. In order to separate any 1-pentene which might be present with the 2-pentene a careful fractionation of the hydrocarbon as an azeotropic mixture was necessary. In view of the contradictory literature data with regard to the boiling point of 1-pentene, a preliminary fractionation in absolute ethyl alcohol through a Hempel column was first made. After two fractionations the hydrocarbon was washed free from alcohol, dried with calcium chloride and refractive indices were taken.

	B. p. of azeotropic mixture with ethyl alcohol at 760 mm., °C.	n_D^{20} of the hydrocarbon	% of total yield
I	32.8–33.1	1.3769	20
II	33.1–33.5	1.3773	21
III	33.5–33.8	1.3780	55
IV	33.8–34	1.3790	2

This fractionation differed markedly from that of the 2-pentene obtained from 3-bromopentane.[2] The ethyl alcohol mixture in that case boiled constantly at 34.7 ± 0.05° and the refractive index of the 2-pentene obtained was n_D^{20} 1.3796. The results of this fractionation indicate the presence of at least two hydrocarbons, one (I) lower boiling occurring in the smaller amount. The main fraction (III) is higher boiling, and II is probably a mixture of I and III. The fact that nothing was obtained higher than 34° would indicate that the 2-pentene (III) is not identical with the 2-peutene obtained from 3-bromopentane. In the continuation of the work the purification of the 2-pentene was made by the repeated fractionation of methyl alcohol mixtures through Crismer columns (50 cm. and 1.5 m. in length). After the third fractionation the separation of 2-pentene from 1-pentene seemed practically complete. Curves I and II in Fig. 1 are typical of various runs and show the difference in the results of a first and third fractionation and also the relative rates of distillation. Practically all of the 1-pentene distilled off in the azeotropic mixture boiling below 30°. It is of interest to compare the values of the hydrocarbons obtained by methyl alcohol fractionation with those given above for ethyl alcohol fractionation.

	B. p. of azeotropic mixture with methyl alcohol at 760 mm., °C.	n_D^{20} of the hydrocarbon	% of the total yield
I	29.9 –30.1	1.37680	15
II	30.75–30.95	1.37849	80
III	30.95–31.2	1.37896	5

B. From 2-Pentanol by the Action of 60% Sulfuric Acid.—The method of Norris and Reuter[4] was employed. The yield from 200 g. of 2-pentanol, fraction boiling at 118–118.5°, n_D^{20} 1.4073 (obtained from material from the Sharples Solvents Corporation), was 146 g. or 92% of the theoretical amount. The crude 2-pentene, washed with sodium hydroxide and dried, was fractionated in methyl alcohol (Curve III, Fig. 1) and the physical constants of the pentene were measured. All of the values, boiling points of azeotropic mixture and of the pure hydrocarbon, the density and the refractive indices were higher than those of the 2-pentene from 2-bromopentane. This was believed to be due to some polymeric material, as found in the case of the preparation of the 2-pentene from 3-pentanol by this method. From the residual alcoholic solution, after fractionation, a rather large amount of material of high index was obtained.



——, I, 2-Pentene from 2-bromopentane, n_D^{20} 1.4416 (753 mm.); – – –, II, 3d fractionation of 2-pentene from 2-bromopentane, n_D^{20} 1.44123 (755 mm.); — · —, III, 2-pentene from 2-pentanol, n_D^{20} 1.4073 (750 mm.).

Fig. 1.—Fractionation of azeotropic mixtures of 2-pentene in methyl alcohol.

Properties of 2-Pentene.—The azeotropic mixture with ethyl alcohol boiled at 33.7 ± 0.2" at 760 mm. The methyl alcohol mixture boiled at 30.85 ± 0.05" at 760 mm. The physical properties of the best 2-pentene prepared from 2-bromopentane considered practically free from 1-pentene are given below with those for the 2-pentene prepared from 3-bromopentane and the 2-pentene formed by the action of light on the latter.

	B. p. (760 mm.), °C.	d_4^{20}	n_D^{20}
2-Pentene from 2-bromopentane	35.85 ± 0.05	0.6481	1.37849
2-Pentene from 3-bromopentane	36.40 ± 0.05	.6503	1.37965
Same 2-pentene after action of light	36.4 ± 0.2	.6500	1.3793

The properties of the 2-pentene prepared from 2-pentanol by sulfuric acid are as follows, with the data given by Norris and Reuter[4] for comparison. This Laboratory data: b. p. 36.15 ± 0.2° at 760 mm ; d_4^{20} 0.6506; n_D^{20} 1.37968; Norris and Reuter data, b. p. 36.39 ± 0.04° at 760 mm.; d_4^{20} 0.65054; n_D^{20} 1.3808. It is also of interest to compare the boiling points of the azeotropic mixtures with methyl alcohol and the refractive indices of other samples of 2-pentene which were not so completely freed from the low-boiling 1-pentene.

	1	2	3
B. p. of azeotropic mixt. (760 mm.)	30.85 ± 0.05°	30.5 ± 0.2°	30.3 ± 0.05°
n^{20}_D of the 2-pentene	1.37849	1.37826	1.37803

Addition Reactions of 2-Pentene.—The possible products of the 2-pentene prepared from 2-bromopentane with hydrogen bromide are 3-bromopentane (n^{20}_D 1.4443) and 2-bromopentane (n^{20}_D 1.4416). In addition, if 1-pentene is present there is also the possibility of 1-bromopentane (n^{20}_D 1.4444). The 2-bromopentane has a lower refractive index, as well as a lower boiling point, than either of the other two. In the case of the addition compounds formed by bromine and 2-pentene there should be only one, the 2,3-dibromopentane; if there is 1-pentene present, however, it would be possible to have some 1,2-dibromopentane. The addition compounds and their boiling points and indices are listed below.

-Bromopentane	3-	2-	1-	2.3-Di-	1,2-Di-
n^{20}_D	1.44431	1.4416	1.4444	1.5074	1.5088 (21°)
B. p., °C.	118.5	117.5	127.9	178	184

Reaction of 2-Pentene with Hydrogen Bromide.—The 2-pentene (prepared from 2-bromopentane), either pure or in a solvent, was placed in a flask surrounded by an ice and salt mixture and saturated with hydrogen bromide. The bromide was washed once with ice water, twice with ice-cold concentrated sulfuric acid, once with ice water, twice with sodium carbonate solution, once with water, dried with calcium chloride and distilled. Typical results are given in Table II. The main product formed by the hydrobromination of 2-pentene is 2-bromopentane nearly 100% pure. In glacial acetic acid the product is about 80–85% 2-bromopentane, but the presence of some 3-bromopentane is indicated by the higher refractive index of the higher-boiling fractions. In the cases where there was the possibility of some 1-pentene being present, the higher boiling point and higher index of the product may be due to the presence of some 1-bromopentane. In some of the addition reactions of hydrogen bromide to this 2-pentene the temperature was not maintained as low as advisable and the results therefore are not as reliable as those made with the isomeric-2-pentene. It is of interest here to note that Norris[4] found that the chief product formed by the addition of hydrogen chloride to 2-pentene was 2-chloropentane.

TABLE II

ADDITION PRODUCTS OF 2-PENTENE

A. 2-Pentene from 2-bromopentane

	2-Pentene, n^{20}_D	Addn. prod. with HBr B. p. at 760 mm., °C.	n^{20}_D		Addn. prod. with bromine B. p. 760 mm., °C.	n^{20}_D	
(1)	1.37849	117–118	1.4416	50%	178	1.5074	
		118–120	1.4418	50%			
(2)	1.37862	118–120	1.4422	75%	178–179	1.5072	86%
		120–123	1.4432	25%	179–184	1.5088	14%
(3)	1.37803	118–119	1.4424	(in hexane)			
		119–120	1.4431	(in hexane)			
		118–119	1.4430	(in glacial	178	1.5078	
		119–120	1.4430	acetic acid)			

B. 2-Pentene from 2-pentanol

(la)	1.37968	117–118	1.4418				
(lb)	1.37942	117–118	1.4425	62%	178–180	1.5079	70%
		118–120	1.4429	38%	180–182	1.5098	30%

Reaction of 2-Pentene with Bromine.—The 2-pentene (prepared from 2-bromopentane) dissolved in either carbon tetrachloride or in glacial acetic acid was cooled in an ice and salt mixture and treated with a solution of bromine in the corresponding solvent as long as the bromine was absorbed. The dibromopentane was washed as in the case of the monobromopentane, dried and distilled. Typical results are given in Table II. In the case of the 2-pentene which from its index of refraction was free from 1-pentene, the dibromopentane seemed to be pure 2,3-dibromopentane; in samples which were believed to contain some 1-pentene there was more or less of a product with a higher boiling point and higher index than the 2,3-dibromopentane, indicating some 1,2-dibromopentane.

Effect of Ultraviolet Light.—Some 2-pentane (from 2-pentanol) was irradiated by ultraviolet light for eight and one-half hours under identical conditions with those used for the 2-pentene prepared from 3-bromopentane.[2] There was a slight increase in the refractive index of the pentene, due in part, perhaps, to polymerization. The monobromopentane formed from the pentene before and after exposure seemed the same, that is, about 93% of 2-bromopentane.

	Exposure to light	
	Before	After
n_D^{20} of 2-pentene	1.37968	1.37989
n_D^{20} of addn. prod. with HBr	1.4418	1.4418

Summary

1. Pentene-2 has been prepared from 2-bromopentane and from 2-pentanol. The pentene has been obtained practically free from 1-pentene by the fractionation of constant-boiling mixtures with methyl alcohol. The 1-pentene is separated in the lower-boiling fractions. The 2-pentene obtained from 2-pentanol by the action of sulfuric acid contains some higher-boiling product which can probably be removed by repeated fractionation of alcoholic mixtures, for a large amount of it remains in the alcoholic residue.

2. The physical properties of the 2-pentene obtained from 2-bromopentane have been determined and have been found to differ slightly from those of the 2-pentene prepared from 3-bromopentane, the former having a slightly lower boiling point, refraction index and density.

3. This 2-pentene (without solvent) adds hydrogen bromide to form 93–95% 2-bromopentane. In a polar solvent such as glacial acetic acid the 2-pentene adds hydrogen bromide to form 85% of 2-bromopentane. It adds bromine to form 2,3-dibromopentane.

4. The action of ultraviolet light on the 2-pentene obtained from 3-bromopentane tends to alter its properties in the direction of those of the isomeric 2-pentene obtained from 2-bromopentane, while the latter isomer remains practically unchanged by ultraviolet light.

5. The differences in physical properties between the two 2-pentenes are such as might be expected in the case of *cis-trans* isomers. The fact,

however, that each isomer has been prepared in a directed manner from a compound of definite and different polarity and that each adds a polar compound in a directed manner corresponding to the method of preparation for each seems to indicate that the two isomers are electronic rather than geometrical. Moreover, the fact that the 2-pentene prepared from 3-bromopentane is transformed into a more stable form is in accord with this theory.

SOUTH HADLEY, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

ISOMERS OF 2-PENTANE. III. THE ULTRAVIOLET ABSORPTION SPECTRA OF THE ISOMERIC 2-PENTENES[1]

BY EMMA P. CARR

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A study of the ultraviolet absorption spectra of the isomeric 2-pentenes prepared by M. I,. Sherrill and co-workers of this Laboratory[2] has been of particular interest in its relation to the electro-isomerism of these compounds and has given further experimental evidence in support of Kharasch's theory of the partial polarity of the ethylene bond.[3] The effect of unsaturation on all of the optical properties of a compound is well known but this effect is particularly marked in the ultraviolet absorption spectra. For example, a 3-cm. length of optically pure hexane transmits to X = 2000 Å. or even further, while the limit of transmission for the same length of pentene is in the region of X = 2600–2800 Å. A quantitative study of the influence of the ethylene group on the infra-red and ultraviolet absorption has been made by Henri,[4] and he shows that, in general, the simple ethylenic compounds have two bands in the ultraviolet, one of very small intensity in the region 2600–2300 Å. and another very intense band in the extreme ultraviolet, X = 2000–1800 Å. These conclusions were based on the investigation of several olefin acids and of allyl alcohol, the *exact* position of the bands due to the double bond being dependent upon the other groups in the molecules. The results of recent spectrographic study of substances in liquid, solution or vapor phase point to the conclusion that ultraviolet absorption is closely related to electronic motion within the molecule and on this basis one would expect that slight differences in the electronic condition of the molecule might be detected by light absorption methods.

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[1] Presented in abstract before the Organic Division at the Swampscott Meeting of the American Chemical Society, September, 1928.

[2] (a) Sherrill, Otto and Pickett, THIS JOURNAL, 51, 3023 (1929); (b) Sherrill, Baldwin and Haas, *ibid.*, 51, 3034 (1929).

[3] M. S. Kharasch and F. R. Darkis, *Chem. Reviews*, 5, 571 (1928).

[4] V. Henri, "Études de Photochemie," Gauthier-Villars, Paris, 1919, p. 98.

The determination of the absorption curves for the isomeric 2-pentenes offered a promising point of attack in the study of electro-isomerism and this investigation was undertaken at the suggestion of Dr. M. S. Kharasch. Since traces of impurities have such a profound effect upon the absorption spectra, the problem resolved itself into the preparation of these isomers in a high degree of purity and it has been only by the constant comparison and checking of absorption measurements with the physical and chemical properties as determined by Sherrill and collaborators[2] that it has been possible to obtain what seems to be confirmatory evidence of the correctness of Kharasch's theory of the electro-isomerism of the 2-pentenes.

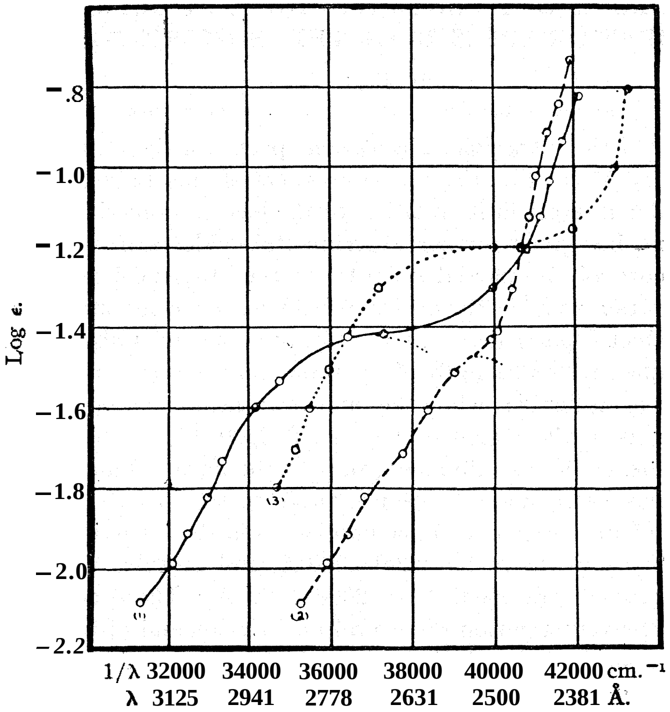

Fig. 1.—(1) ——, 2-Pentene prepared from 2-bromopentane, n_D^{20} 1.37849; (2) – – –, 2-pentene prepared from 3-bromopentane, n_D^{20} 1.37945; (3) ...., trimethylethylene according to Lüthy [*Z.* physik. *Chem.*, 107,285 (1923)].

Our results show that the absorption curve for the 2-pentene prepared from 3-bromopentane differs markedly from that of the 2-pentene obtained from 2-bromopentane (Fig. 1). The absorption curves of these two isomers are so characteristic that they have given a most delicate method of identifying these isomers as well as of differentiating them from 1-pentene and the polymeric forms of 2-pentene which may be present as impurities. The absorption spectrum of trimethylethylene has been measured by Lüthy[5] and that part of the curve in the region in which the 2-pentenes were examined has been reproduced in Fig. 1. A marked "step-out" in the general absorption of a substance indicates an absorption band of such small persistence that the complete band is not evident and such a step-out is shown by all of the pentenes in the region λ 2700–2500 Å.

The curves for the stable 2-pentene (Curve 1, Fig. 1) and trimethylethylene (Curve 2, Fig. 1) are almost exactly similar in form and differ only in the position of the band and to a slight degree in intensity,[6] whereas the curve for the isomeric 2-pentene prepared from 3-bromopentane is very different. The broad step-out has disappeared entirely and there is only the slightest tendency toward an absorption band. In the longer wave lengths this isomer transmits farther; in the shorter wave lengths slightly less. The differences are striking and of great interest in connection with the possibility of the electro-isomerism of the 2-pentenes. The shallow absorption band in this region is characteristic of all ethylenic compounds and if this absorption band is related to the second pair of electrons, the so-called labile pair, in the double bond it would be in this band that one would expect differences in the absorption of electronic isomers to be most evident and there should be little or no difference in the second band in the far ultraviolet. In this connection it is of interest to note that in seven pairs of *cis-trans* isomers which ham been examined by quantitative methods[7] the two forms have very similar absorption curves but the *trans* form is somewhat more absorptive and this difference becomes *much more marked* the shorter the wave length. It would seem, therefore, that with geometrical isomerism it is the intense band in the far ultraviolet which differs with the two isomers while in electro-isomerism it is the band of low intensity in the near ultraviolet which shows the marked differences. Although experimental data are too meager to justify far-reaching conclusions, these results certainly suggest the possibility that the absorption band in the far ultraviolet is related to the characteristic frequency of the stable pair of electrons in the double bond and these electrons are primarily concerned in *cis-trans* isomerism, while the second pair of electrons, being much more labile, produce the shallow band of much lower frequency and, according to the theory of Kharasch, it is the relative position of this pair of electrons which determines electronic isomerism.[3]

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[5] Lüthy, Z. *physik.* Chem., **107,** *285* **(1923).**

[6] Repetition of the work on trimethylethylene in this Laboratory corroborates Lüthy's measurements as to the position of the band but shows the step-out at log $\epsilon = -1.4$ instead of -1.2.

[7] Errera and Henri, *Compt. rend.,* **181, 548 (1925).**

The absorption curves for different preparations of 2-pentene prepared from 3-bromopentane by the action of alcoholic potassium hydroxide and from 3-pentanol by the action of 60% sulfuric acid are given in Fig. 2. The solid line curve gives results for three completely independent preparations of 2-pentene made from different samples of synthetic 3-bromopentane. The broken line curves show the absorption of 2-pentene prepared from synthetic 3-bromopentane which, from its index of refraction, contained some 2-bromopentane. Where the index of refraction shows a mixture of 2- and 3-bromopentane the absorption curve of the pentene prepared from the mixture indicates at once that the product is a mixture of the two isomeric 2-pentenes, (Curves 2 and 2′, Fig. 2) and calculations of the relative amounts of the two isomers on the basis of the extinction coefficient as a linear function of the concentration, give very satisfactory agreement with those calculated from the index of refraction of the mixture. The fact that these results are in agreement also with those obtained from the addition of hydrogen bromide to the pentene

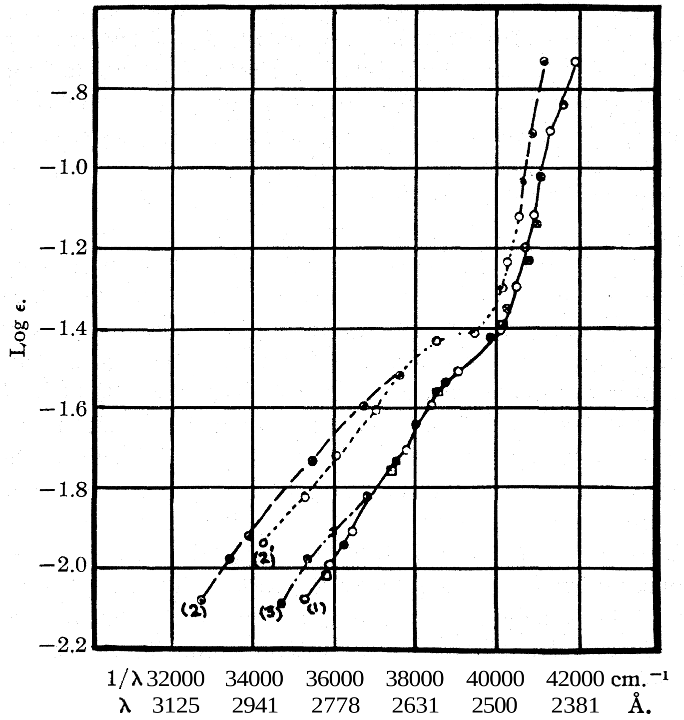

Fig. 2.—Different preparations of 2-pentene. (1) From 3-bromopentane, ○, n_D^{20} 1.37945; ● n_D^{20} 1.37965; □ n_D^{20} 1.37965. (2) From 3-bromopentane, ⊙ n_D^{20} 1.37923; ○ . . ., n_D^{20} 1.37909. (3) From 3-pentanol (synthetic), ⊗, n_D^{20} 1.37935.

and analysis of the mixture of bromopentanes has established confidence in the accuracy of our conclusions. In all preparations of 2-pentene which were made directly from the alcohol there is a small amount of a more absorptive material which is evidenced by a slightly increased absorption in the longer wave lengths. Inasmuch as sulfuric acid increases the polymerization of the olefins and the higher-boiling fractions contain a greatly increased amount of this more absorptive material and have a correspondingly higher index of refraction, the increased absorption is no doubt due to the presence of polymeric forms of the pentene. The delicacy of the spectrographic method of examination is shown in Fig. 3, where a difference in boiling point of three-tenths of a degree in the azeotropic mixtures gives an enormous difference in absorption, although the increase in index of refraction is comparatively slight. No such striking increase in the absorption of the higher fractions of 2-pentene obtained from the bromopentanes was found since the tendency to polymerize is very much less when prepared by alcoholic potash than by the action of sulfuric acid.

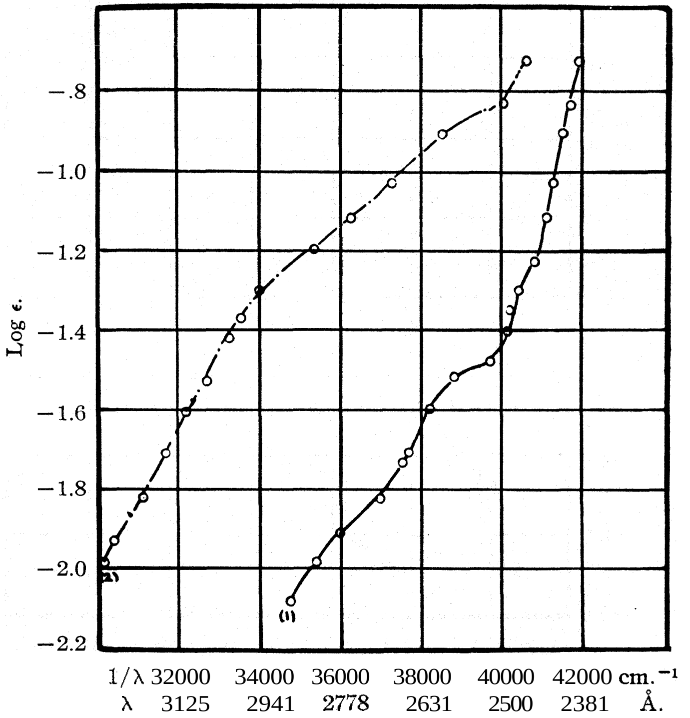

Fig. 3.—Fraction of 2-pentene from 3-pentanol. (1) Azeotropic mixt. with CH_3OH, b. p. 30.9–31.1°; C_5H_{10} n_D^{20} 1.37935. (2) Azeotropic mixt. with CH_3OH, b. p. 31.1–31.5°; C_5H_{10} n_D^{20} 1.37988.

In the preparation of the 2-pentene from 2-bromopentane and 2-pentanol, small amounts of 1-pentane are formed and by means of absorption spectra measurements it was possible to follow the separation of these isomers. Figure 4 shows the absorption curves of the different fractions in the distillation of a methyl alcohol solution of 2-pentene prepared from 2-bromopentane. Results from bromination and hydrobromination data[2b] showed that the low-boiling fraction contained the 1-pentene, and the absorption curve for the fraction (Curve 1) shows greater transmission than either of the 2-pentenes.[8]

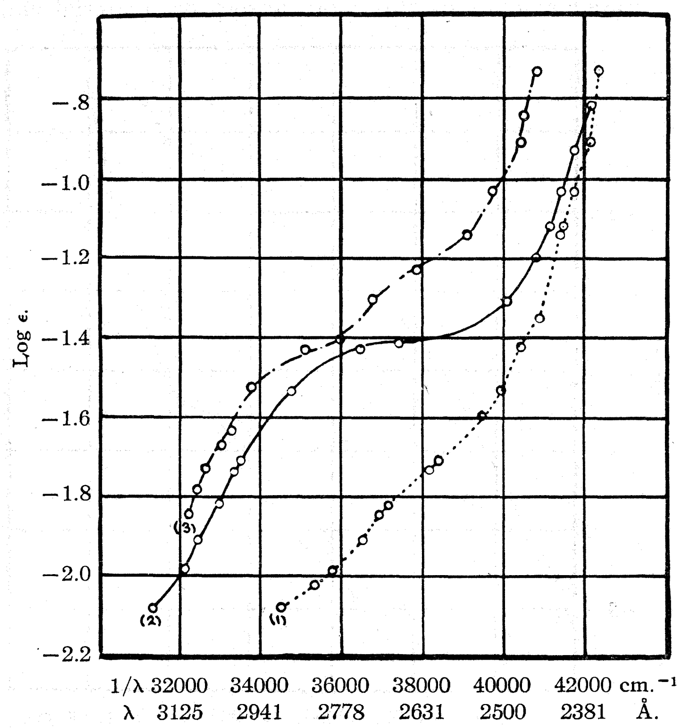

Fig. 4.—Fractionation of 2-pentene prepared from 2-bromopentane. (1) Azeotropic mixt. with CH_3OH, b. p. 29.9–30.1°; C_5H_{10}, n_D^{20} 1.37680. (2) Azeotropic mixt. with CH_3OH, b. p. 30.75–30.95°; C_5H_{10}, n_D^{20} 1.37849. (3) Azeotropic mixt. with CH_3OH, b. p. 30.95–31.5°; C_5H_{10}, n_D^{20} 1.37876.

The effect of diffused light on the absorption spectrum of the 2-pentene prepared from 3-bromopentane is shown in Fig. 5. The solid line (Curve

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[8] A recent preparation in this Laboratory of 1-pentene confirms the low boiling point and index of refraction, but the 1-pentene contains traces of allyl bromide from which it was prepared. This impurity increases the absorption tremendously but even so the preparation transmits further than either of the 2-pentenes, thus confirming our conclusion that the low-boiling fraction is 1-pentene.

1) gives the absorption of the original material and the broken line (Curve 2) that of the same material after standing in a sealed glass tube and exposed to the diffused sunlight of the laboratory for three months. In comparison with the absorption curve of the 2-pentene from 2-bromopentane (Curve 3), which according to Kharasch should be the stable form, this light-transformed material shows the presence of a more absorptive

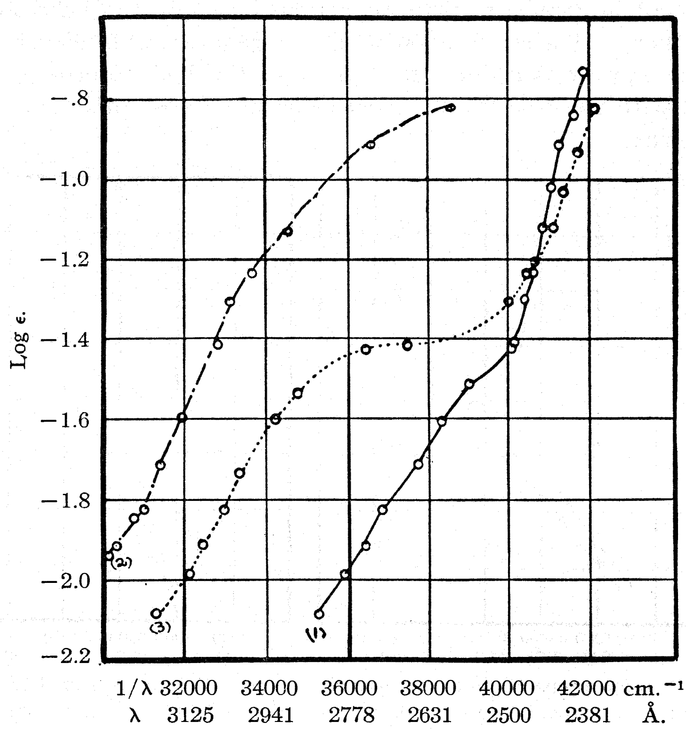
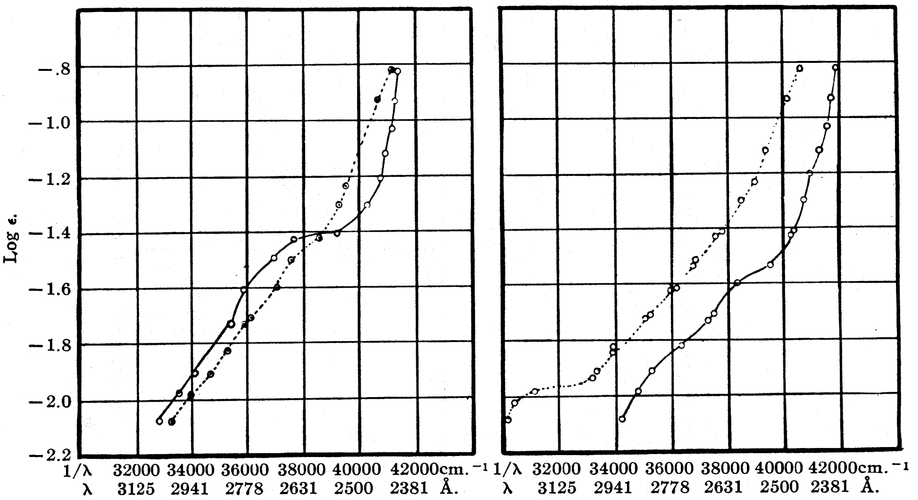


Fig. 5.—(1) ——, 2-Pentene prepared from 3-bromopentane, n^{20}_{D} 137965; (2) —·—, 2-pentene after 3 months in sunlight and diffused light, n^{20}_{D} 1.37934; (3)......., 2-pentene prepared from 2-bromopentane, n^{20}_{D} 1.37849.

material of higher index of refraction. The most probable conclusion, and one which is in accord with results of hydrobrominating this substance, is that this curve represents a mixture of the isomeric 2-pentene together with a small amount of the very absorptive polymer.

The study of the absorption curves of the two isomeric pentenes before and after exposure to ultraviolet light from the mercury arc for eight and a half hours shows an opposite effect of light on the two isomers (Fig. 6). The 2-pentene prepared from 2-pentanol shows much greater stability and the absorption is shifted only very slightly toward the ultraviolet, whereas the absorption of the 2-pentene from 3-bromopentane is shifted toward the visible and a new band in the region of λ = 3125 Å. indicates a decomposition with the formation of a new substance.

The study of the progressive action of light on these isomers is being continued in this Laboratory and the results so far obtained give strong support to our conclusion that the two isomers are electromers. Their relative stabilities are in accord with the postulates of Kharasch's theory and are not in agreement with predictions based on the behavior of *cis-trans* isomers. The usual action of light on geometrical isomers is to transform the more absorptive trans-form into the less absorptive *cis-form,* whereas with the isomeric 2-pentenes the more absorptive isomer is the stable form.

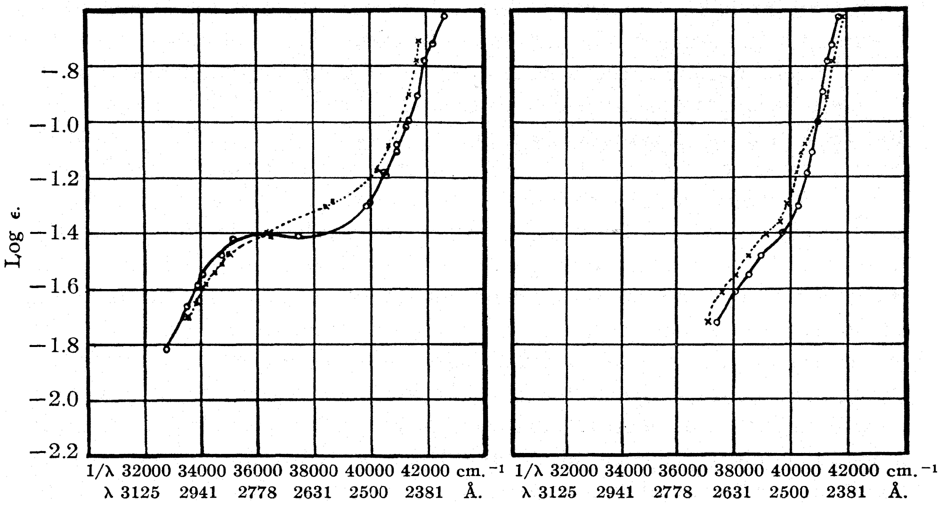


——, 2-Pentene prepared from 2-pentanol, n_D^{20} 1.37968; - - - -, 2-pentene after exposure to ultraviolet light for 8.5 hours, n_D^{20} 1.37989.

——, 2-Pentene from 3-bromopentane, n_D^{20} 1.37930; - - - -, 2-pentene after exposure to ultraviolet light for 8.5 hours, n_D^{20} 1.37956.

Fig. 6.—Action of ultraviolet light on the 2-pentenes.

Inasmuch as the relative amounts of 3-bromopentane and 2-bromopentane obtained by hydrogen bromide addition to the 2-pentenes are dependent upon the solvent used, it is of interest to compare the absorption spectra of each of the 2-pentenes when photographed in a non-polar solvent such as hexane and in a polar solvent, glacial acetic acid. V. Henri and his collaborators, in a long series of investigations of the ultraviolet absorption spectra of organic substances in vapor phase and in various solvents, have shown that the absorption curve in hexane solution most closely resembles that in the vapor phase and have regarded the absorption curve in hexane as the "normal" spectrum. Our results show a very slight shift in intensity between the curves of the pure liquid pentene and its hexane solution, due no doubt to the difficulty in determining the exact concentration of the solution of the very volatile 2-pentene. In order to study the absorption spectrum in the region of the "step-out" it was necessary to use very concentrated solutions, as the intensity of this band is too small to measure in dilute solution. Solutions of each isomer in hexane and in glacial acetic acid were made up in the ratio of three volumes of pentene to one volume of solvent and the molar concentration was calculated from the density determinations. The absorption curves for these solutions are given in Fig. 7. With each isomer the curve for the hexane solution coincides practically with that obtained from the examination of the liquid pentene, but in glacial acetic acid the curve for the 2-pentene which had been prepared from 2-bromopentane is shifted slightly toward that of the isomeric 2-pentene and that of the second isomer prepared from 3-bromopentane is shifted toward the curve for the first isomer. These results in acetic acid solution are surprising in that they involve, in the curve for one isomer, a shift of absorption toward the ultraviolet end of the spectrum in the longer wave lengths and toward the visible in the shorter wave lengths. With the other isomer the shift in absorption is exactly opposite and these results are in complete agreement with predictions based on hydrogen bromide addition to the two isomers.[2] When hydrogen bromide gas is added to the 2-pentene prepared from 2-bromopentane either without any solvent or in a non-polar



2-Pentene prepared from 2-bromopentane; ——, 2-pentene dissolved in hexane; ......, 2-pentene dissolved in glacial acetic acid.

2-Pentene prepared from 3-bromopentane; ——, 2-pentene dissolved in hexane; ...., 2-pentene dissolved in glacial acetic acid.

Fig. 7.

solvent the product is 98–100% 2-bromopentane; with the other isomer the product is 98–100% 3-bromopentane.

The absorption curves in hexane give no evidence of any change in electronic condition brought about by the solvent and on this basis, if the isomers are electronic, addition of hydrogen bromide in a non-polar solvent would give 100% 2-bromopentane or 100% 3-bromopentane, as the case might be. Further, if the isomers are electronic a polar solvent such as glacial acetic acid would give a different electrical environment with a consequent effect on the relative position of the pair of labile electrons and therefore of the polarity of the double bond. In the addition of hydrogen bromide this electronic shift would be indicated by a change in the relative amounts of 2-bromo- and 3-bromopentane obtained; addition of hydrogen bromide to the 2-pentene obtained from 3-bromopentane when the pentene is dissolved in glacial acetic acid gives 78% of 3-bromopentane and 28% of 2-bromopentane; addition to the other isomer of 2-pentene in glacial acetic acid gives 85% of 2-bromopentane and 15% of 3-bromopentane. In ultraviolet absorption the effect of the polar solvent should be most evident in the region of the spectrum where the absorption is directly related to the characteristic frequency of the pair of labile electrons. Our spectrographic results so far all point to the conclusion that the band at λ2500–2700 Å. is due to the electronic motion of the second or labile pair of electrons in the double bond and it is exactly here that the pronounced changes in the absorption curves of the acetic acid solutions are shown.

Although no one piece of evidence is completely conclusive in itself in establishing the electro-isomerism of the 2-pentenes, the complete agreement of results based on methods of preparation, directive addition of hydrogen bromide and ultraviolet absorption spectra make such a conclusion the most reasonable interpretation. The differences in physical properties of the two isomers, although slight, certainly indicate two distinct substances. Kharasch and Darkis[3] have pointed out that there are no experimental data which would justify the assumption that cis-*trans* isomers add an unsymmetrical reagent in a different manner and base their conclusions on the electro-isomerism of the 2-pentenes before and after exposure to light on the change in the directive addition of hydrogen bromide. Independent confirmation of their theory is obtained in the preparation by Sherrill and collaborators in this Laboratory of two isomeric 2-pentenes from either 3-bromopentane or 3-pentanol and from 2-bromopentane. Since these preparations were from substances which differed primarily in their electronic structure due to the difference in position of the electronegative bromine atom, or hydroxyl group, it is reasonable to expect that the pentenes formed would differ in electronic structure, but there is no reason to predict or expect a different spatial configuration as in geometrical isomerism.

In the spectrographic study of geometrical isomers the *trans* form, which is the less stable in light, is more absorptive than the cis form. In the 2-pentenes the isomer which is less stable in light is the less absorptive. *Cis-trans* isomers show their marked differences in absorption in the far ultraviolet; the 2-pentenes show their marked differences in the near ultraviolet. In the study of the 2-pentenes there has been no experimental result which is not readily explained on the basis of electronic isomerism, whereas a number of results cannot be reconciled with the previously established behavior of geometrical isomers.

Experimental

The absorption spectra measurements were made by means of a Hilger quartz spectrograph (E2) using an iron spark as a source of light. The sparking apparatus consisted of a 0.25 kilowatt transformer and condenser of approximately 0.03 m. f. capacity as recommended by Hilger for spectrum work. The rectangular iron electrodes, cross-section 2 mm. by 3 mm., were carried in a holder with vertical and horizontal adjustment and the width of the spark-gap was kept at 2 mm. Measurements of the absorption were made in small Baly absorption tubes of clear fused quartz with optically worked ends fused to the tube and with ground quartz connections such that the length of absorbing liquid could be adjusted without the use of the ordinary rubber connections. This avoidance of rubber and also of cement for fastening the quartz plates to the tube was of great advantage in maintaining the purity of the liquids under examination. The length of the absorbing medium was varied from 70 mm. to 4 mm. Lumière and Jougla photographic plates were used throughout the investigation. The extinction coefficients were determined by the photographic method of comparison spectra developed by Henri.[9]

The intensity of the incident light was varied by varying the time of exposure and a uniform time of ten seconds was adopted for photographing the spectrum of the solvent. Between each two spectra of the solution exposed for forty seconds and sixty seconds, respectively, was photographed the spectrum of the solvent through the same thickness, for ten seconds. The duration of the exposure was carefully timed and for the times which were used the validity of Schwarzschild's law has been accurately established

$$\frac{I_0}{I} = \left(\frac{t}{t_0}\right)^n$$

where I_0 is the intensity of the incident light; I, the intensity of the transmitted light; t_0 is the time of exposure through the solvent of a given thickness; t, the exposure time through the solution of the same thickness, and n, a constant dependent on the photographic plates used. The

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[9] Ref. 4, p. 5.

value of this constant was checked in this Laboratory by comparison with the absorption curve of potassium chromate in 0.05 N potassium hydroxide.[10] Extinction coefficients for this curve were determined both by photoelectric and different photographic methods and the close agreement of our results checked not only the value of the constant for the photographic plates but gave a very satisfactory check on the accuracy of our experimental procedure.

A Leitz binocular was used for determining the points of equal density between the spectra of solution and solvent of the same thickness and the wave lengths were identified from the known wave lengths of the iron spark. By combining Schwarzchild's law with the Bunsen-Roscoe law, which defines the extinction coefficient, $\epsilon = 1/cd \log I_0/I$, and substituting the value of $n = 0.9$, the extinction coefficients can be calculated from the experimental data by the following formula

$$\epsilon = \frac{0.9}{\text{cd}} \log \frac{t}{t_0}$$

where c is the concentration in moles per liter, d is the thickness in cm., t is the exposure time for solution, and t_0 for solvent.

Where the absorption spectrum of the pure liquid pentene was photographed, the molar concentration was calculated from the density and as a comparison spectrum the spark through the same thickness of optically pure hexane was used rather than the spark alone, since the density of hexane (0.660) is close to that of the pentene (0.650). In determining the effect of solvent on the absorption spectra of the 2-pentene, very concentrated solutions were used for two reasons: first, such concentrated solutions are necessary in order to obtain the region in which the band of low intensity is found; second, glacial acetic acid is itself quite absorptive and solutions containing too large proportions of the acid would not transmit sufficiently far to study the region in which this shallow band appears. Two cc. of solvent was added to 6 cc. of pentene and the molar concentration was calculated from the density. A solution of 2 cc. of glacial acetic acid in 6 cc. of hexane was used for the comparison spectrum with the acetic acid solutions of the 2-pentenes.

The optical purity of the solvent in spectrographic work is of the greatest importance and methods of purification of organic solvents have been worked out in Henri's laboratory.[11] One liter of hexane from petroleum (b. p. 65-70°) was shaken for twelve hours with 150 cc. of fuming sulfuric acid (10%), the hexane was decanted and this process was repeated twice with fresh amounts of fuming sulfuric acid. It was then shaken for twelve hours with 150 cc. of concentrated sulfuric acid (sp. gr. 1.84), washed twice with distilled water and shaken for another twelve hours each with (1) 150 cc. of 10% sodium carbonate solution, (2) 150 cc. of a mixture containing 100 cc. of normal potassium permanganate and 50 cc. of 10% sodium carbonate and (3) 150 cc. of a mixture containing 50 cc. of 10% sulfuric acid and 100 cc. of normal potassium permanganate. The hexane was then decanted, washed several times with water,

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[10] Weigert, "Optische Methoden der Chemie," Akademische Verlagsgesellschaft, Leipzig, 1927, p. 236; Roszler, *Ber.*, 59, 2608 (1926); Scheibe, May and Fischer, *ibid.*, 51, 1332 (1924).

[11] Castille and Henri, *Bull. soc. chim. biol.*, 6,299 (1924); A. Iuthy, ref. 5; Weigert, ref. 10, p. 212.

dried over sodium wire and distilled with a fractionating column. The hexane thus prepared transmitted the copper line λ 2105 Å., which is the limit of transmission of this type of spectrograph. The glacial acetic acid was purified by repeated recrystallization of the c. p. glacial acetic acid obtained from the General Chemical Company. The 2-pentenes were thoroughly dried over fused calcium chloride before spectrographic examination.

Summary

The ultraviolet absorption spectra of the 2-pentene prepared from 3-bromopentane or 3-pentanol and of the 2-pentene from 2-bromopentane or 2-pentanol show marked differences, particularly in the region of the shallow absorption band in the near ultraviolet. The absorption curves of the two isomers are so characteristic that they have given an excellent method of identifying these isomers as well as of differentiating them from 1-pentene and the polymeric forms of 2-pentene which may be present as impurities.

The effect of a polar solvent, glacial acetic acid, as compared with the non-polar solvent, hexane, on the absorption spectra of the two isomeric 2-pentenes shows that the acetic acid in each case shifts the absorption slightly toward that of the other isomer, while in hexane solution each curve is almost identical with that for the corresponding pure liquid pentene. These results are in accord with the addition reactions of the isomeric pentenes in the two solvents and indicate the existence of electronic isomers. In a non-polar solvent each isomer retains its identity; in a polar solvent there is an electronic shift with the consequent formation of some of the other isomer.

Absorption spectra measurements of the 2-pentene from 3-bromopentane before and after prolonged exposure to diffused light show a shift in the absorption corresponding to a transformation into the isomeric 2-pentene, together with the formation of some more absorptive polymer. When exposed to the ultraviolet light from the mercury arc for eight to nine hours, the absorption spectrum of 2-pentene obtained from 3-bromopentane or 3-pentanol shows a decided shift of the absorption toward the visible, while the isomeric 2-pentene from 2-bromopentane or 2-pentanol under identical conditions is quite stable and shows only a very slight shift of absorption in the opposite direction, that is, toward the absorption curve of the isomeric 2-pentene.

The results of the spectrographic examinations of the isomeric 2-pentenes are in accord with the interpretation of electronic isomerism as proposed by Kharasch, but are not in agreement with the previously established behavior of geometrical isomers.

SOUTH HADLEY, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MCLAUGHLIN GORMLEY KING COMPANY]

STUDIES ON PYRETHRUM FLOWERS. I. THE QUANTITATIVE DETERMINATION OF THE ACTIVE PRINCIPLES

BY C. B. GNADINGER AND C. S. CORL

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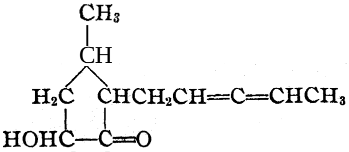
Although the insecticidal properties of *Pyrethrum* flowers have been known for more than a century, no satisfactory method has existed for the determination of the toxic principles. During the last five years the use of *Pyrethrum* has grown enormously, because of the development of new types of liquid insecticides, and the need for a method for evaluating the flowers has increased correspondingly. Of the methods in use prior to 1927,[1] only the physiological tests on insects give results that indicate the comparative value of different samples. These tests are difficult to conduct under constant conditions and are, at best, inaccurate. The chemical methods, involving the determination of ash constituents, ether-extract, nitrogen, etc., afford no idea of the amount of toxic principles present.

Staudinger and Harder[2] have published a method that is an adaptation of the process originally used by Staudinger and Ruzicka,[3] for the isolation of the active principles of *Pyrethrum*. This method is long, tedious and difficult to conduct quantitatively, requiring 500 g. of sample for a single determination.

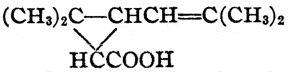
The purpose of this paper is to describe an accurate and comparatively rapid chemical method for determining the percentage of active principles in *Pyrethrum* flowers.

Experimental Part

Preparation of the Pure Active Principles.—In 1916 Staudinger and Ruzicka[4] isolated the toxic principles of *Pyrethrum* and definitely established their composition and structure. The two toxic substances, which they named pyrethrin I and pyrethrin II, were shown to be esters of the ketone-alcohol pyrethrolon with two acids, chrysanthemum monocarboxylic acid and chrysanthemum dicarboxylic acid methyl ester. Since these compounds will be referred to frequently throughout this paper, their structural formulas, as determined by Staudinger and Ruzicka, are given herewith



Pyrethrolon



$(CH_3)_2C{-}CHCH{=}C(CH_3)_2$, $HCCOOH$

Chrysanthemum monocarboxylic acid

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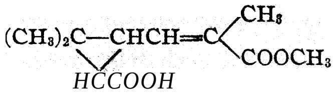
[1] "Insect Powder," U. S. Department of Agriculture Bulletin No. 824 revised.

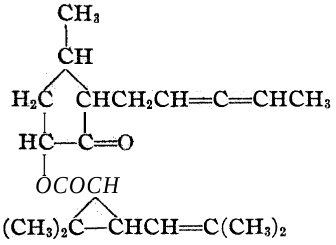
[2] Staudinger and Harder, *Ann. Acad. Sci. Fennicae,* **29A,** 1–14 (1927).

[3] Staudinger and Ruzicka, *Helv. Chim. Acta,* 7, 177–201 (1924).

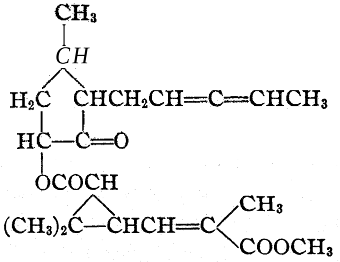
[4] Staudinger and Ruzicka, *ibid.,* 7, 177–259,377458 (1924).



Chrysanthemum dicarboxylic acid methyl ester



Pyrethrin I



Pyrethrin II

By using a modification of the method of Staudinger and Ruzicka, quantities of nearly pure pyrethrin I and pyrethrin II were prepared from the best quality of Japanese *Pyrethrum (Chrysanthemum cinerariaefolium* Bocc.). For this purpose 680 kg. of the flowers was ground to 30-mesh and extracted with 3800 liters of acetone. The acetone was removed by distillation *in vacuo,* and there remained 90 kg. of oleo-resin of *Pyrethrum.* This material was worked up in small portions because of the difficulty of handling the large volumes of solvents required in the process. For example, the last portion was treated in the following manner: 6.5 kg. of the oleo-resin (corresponding to 49.1 kg. of flowers) was dissolved in 10 liters of acetone and mixed with 15 liters of low-boiling petroleum ether. A large amount of gummy material separated and it was washed with 8 liters of ether and then with 8 liters of benzene. The insoluble residue, which weighed 3120 g., contained only 2.96 g. of pyrethrins and was discarded. The mixture of solvents, containing the main portion of pyrethrins, was distilled *in vacuo* to 4 liters and was poured into 16 liters of petroleum ether. A further separation of green, semi-solid material occurred; it weighed 1680 g., contained 77.76 g. of pyrethrins and was discarded. The petroleum ether solution was distilled *in vacuo* and the residue was poured into 4 liters of methanol. The fatty material that separated was washed four times with 1-liter portions of methanol. The methanol-insoluble fat weighed 640 g. and contained 5.60 g. of pyrethrins. The methanol solution was chilled at −7° until no further precipitation took place and the fatty precipitate weighing 90 g. was filtered off; it contained 9.74 g. of pyrethrins. The methanol solution was distilled *in vacuo* to a volume of 2500 cc. and sufficient water was added to make the alcohol content 88%. The solution was chilled overnight and the fatty material that separated was washed three times with 1-liter portions of 90% methanol. This insoluble fat weighed 260 g. and contained 13.31 g. of pyrethrins. All of the fatty residues were discarded. The methanol solution was distilled *in vacuo* and the residue was dissolved in petroleum ether. The petroleum ether solution was filtered from the 149 g. of insoluble material that contained only a trace of pyrethrins and was distilled in *vacuo.* The oily residue from the petroleum ether distillation weighed 548 g. and contained 304 g. of pyrethrins. In addition to the 304 g. of pyrethrins recovered in impure condition, 109 g. was lost in the process. Thus the total pyrethrin content of the 49.1 kg. of flowers was 413 g., or 0.84%. Subsequently, analysis of the same lot of flowers showed a pyrethrin content of 0.87%.

The oil containing 55.5% of pyrethrins was further purified by treatment with sodium carbonate solution and basic lead acetate. The pyrethrins were then converted into their semicarbazones by the method described by Staudinger and Ruzicka;[5] 288

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[5] *Cf.* ref. 4, p. 190.

g. of the oil yielded 220 g. of the impure, mixed semicarbazones of pyrethrin I and pyrethrin II.

The semicarbazone of pyrethrin I was separated in nearly pure condition (m. p. 117–119°) by repeated crystallization of the crude mixture from benzene and alcohol. The pure semicarbazone of pyrethrin II could not be isolated, but after fifty-one crystallizations from benzene, alcohol and mixtures of benzene and petroleum ether, a semicarbazone was obtained that melted at 56–59°. Both semicarbazones crystallized from benzene in white needles. A large amount of mixed pyrethrin semicarbazones melting at 70–90° was also obtained.

By heating the semicarbazones with oxalic acid solution,[6] they were converted into the corresponding pyrethrins. The crude pyrethrins were extracted from the oxalic acid solution with petroleum ether and washed free from acids with 1% sodium hydroxide solution. Further purification was effected by washing with 3% chromic acid solution and 3% potassium permanganate solution, which did not attack the pyrethrins appreciably. The petroleum ether was then removed *in vacuo* and the residue was dissolved in alcohol, whereby a small amount of insoluble matter was precipitated. The alcohol solution was filtered and distilled in *vacuo*, the residue was dissolved in petroleum ether and the solution was filtered and distilled in *vacuo* at a maximum temperature of 55° until constant weight was attained. Ten grams of semicarbazone of pyrethrin I (m. p. 117–119°) yielded 3.53 g. of pure pyrethrin I; 10 g. of semicarbazone of pyrethrin II (m. p. 56–59°) yielded 2.76 g. of nearly pure pyrethrin II.

Anal. Calcd. for $C_{21}H_{30}O_3$ (pyrethrin I): *C*, 76.31; H, 9.16. Found: C, 75.95, 76.36; H, 9.32, 9.06. Calcd. for $C_{22}H_{30}O_5$ (pyrethrin II): C, 70.54; H, 8.08. Found: C, 72.71; H, 8.18.

In the course of this work it was noticed that when a drop of solution containing the pyrethrins was applied to the tongue, a very marked numbing effect was produced. Eventually it was proved that the sensation was caused by pyrethrin I and pyrethrin II. The numbing or tingling sensation was much the same as that produced by rubbing the tongue with aconite root. With pyrethrins the numbness developed five or ten minutes after placing on the tongue, and the effect persisted for one to three hours.

Toxicity of the Pyrethrins to Insects.—The insecticidal activity of the isolated pyrethrins was determined by experiments on cockroaches (*Blatta germanica*). One of us had observed that an acetone or alcohol

TABLE I

TOXICITY OF THE PYRETHRINS TO COCKROACHES

composition of solution tested				
Pyrethrin,	mg.	Water, cc.	Ratio pyrethrin:water	Cockroaches dead in 24 hours, %
I	33	1000	1:30,300	100
I	20	1500	1:75,000	100
I	12.5	1000	1:80,000	100
I	20	2000	1:100,000	50 Balance disabled
I	20	3000	1:150,000	None dead; all disabled
II	33	1000	1:30,000	100
II	20	1500	1:75,000	100
II	12.5	1000	1:80,000	50 Balance disabled
II	20	2000	1:100,000	50 Balance partly disabled
II	20	3000	1:150,000	None dead; all recovered

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[6] Cf. ref. 4, p. 194.

solution of pyrethrins, when diluted with water, forms a stable colloidal suspension of great insecticidal power.' Por the experiments with cockroaches the pyrethrins were dissolved in alcohol and then diluted with water to the desired strength. The amount of alcohol in the solution applied to the cockroaches was less than 0.5%. The dilute solutions were freshly prepared before each experiment and the pyrethrins remained uniformly distributed without settling or floating. The results of the experiments are given in Table I.

Pyrethrin I was slightly more active than pyrethrin II, as Staudinger and Ruzicka have noted. The pure pyrethrins were extremely toxic to cockroaches.

Reducing Action of the Pyrethrins on Alkaline Copper Solution.—Staudinger and Ruzicka have mentioned that pyrethrolon reduces alkaline copper solution. It was found that pyrethrin I and pyrethrin II have the same property and the idea of using the reaction for determining the pyrethrins at once suggested itself. The copper reducing power of the pyrethrins was found to be considerably less than that of dextrose and the other reducing sugars, and for this reason the gravimetric sugar methods could not be applied satisfactorily. Of the other sugar methods, the colorimetric method of Folin,[8] for determining dextrose in blood, seemed to be the most promising. In this method a measured amount of specially treated blood is heated with an alkaline copper solution, in a tube designed to prevent oxidation of the precipitated cuprous oxide. A tube containing a known amount of dextrose is treated in precisely the same manner. When the heating is finished, the Folin phosphomolybdate reagent is added to the tubes and a deep blue color is developed by the action of the cuprous oxide on the phosphomolybdate solution. The intensities of the colors are compared and the amount of dextrose in the blood is calculated in the usual way.

In a long series of experiments this method was adapted to the determination of pure pyrethrins in alcoholic solution. A special size of Folin sugar tube was used because oxidation of the reduced copper took place rapidly when test-tubes were used as suggested by Benedict.[9] Several modifications of Folin's reagent were tried and a large number of alkaline copper solutions were investigated. The effects of varying the temperature and time of the reaction were noted. More than 700 experiments were made before the best procedure for conducting the test was determined.

Comparisons of the colors produced by known amounts of the pyrethrins with those obtained from known amounts of dextrose, indicated that dextrose could be used as a standard, as in the Folin method. The ratio of the pyrethrin used to the copper reduced was not a constant. A number

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[7] Patent applied for by C. B. Gnadinger, July 6, 1926.

[8] Folin, *J. Biol. Chem.*, 67, 357–370 (1926).

[9] Benedict, *ibid.*, 64, 207–213 (1925).

of comparisons were made between different quantities of pyrethrins and a constant amount of dextrose; the results of these experiments were plotted. The curves were not linear functions, but more nearly conformed to the parabolic equation used by Allihn[10] in his work on dextrose. In Table II the amounts of dextrose equivalent in copper reducing power to different quantities of pyrethrin I and pyrethrin II are given. These ratios were obtained by comparing the color produced by 2 mg. of dextrose with the colors yielded by the different weights of pyrethrins; the method by which these comparisons were made will be described later.

TABLE II

COMPARISON OF COPPER REDUCING POWER OF DEXTROSE AND PYRETHRINS

Weights having equivalent copper reducing power									
Pyrethrin I, mg.	Dextrose, mg.				Av., mg.	Pyrethrin II, mg.	Dextrose mg.		Av., mg.
5.0	0.735	0.767	0.787	0.797	0.772	..	...	...	...
7.5	1.166	1.175	1.228	1.246	1.204	7.5	0.973	1.003	0.988
12.5	2.020	2.036	2.046	2.061	2.041	12.5	1.636	1.642	1.639
15.0	2.222	2.222	2.253	2.292	2.247	15.0	1.956	1.980	1.968
17.5	2.469	2.500	2.500		2.489	17.5	2.253	2.272	2.263
20.0	2.730	2.826	2.836		2.797	20.0	2.402	2.539	2.471

By substituting the values in Table II in the equation $y = a + bx + cx^2$, (where y = mg. of dextrose, x = mg. of pyrethrin, and a, b and c are constants) and applying the method of least squares, two equations were obtained

Eq. I (for pyrethrin I): $y = -0.2536 + 0.2237x - 0.00365x^2$
Eq. II (for pyrethrin II): $y = -0.0101 + 0.1437x - 0.0009x^2$

From these equations the dextrose equivalent to the quantities of pyrethrins in Table II was calculated; the observed and calculated values are compared in Table III, where the ratio of the reducing power of pyrethrin I to that of pyrethrin II also appears.

TABLE III

OBSERVED AND CALCULATED RESULTS AND COMPARATIVE REDUCING POWER OF PYRETHRINS I AND II

Pyrethrin, mg.	Dextrose equiv. to Py. I Obs., mg.	Calcd., mg.	Diff., mg.	Dextrose equiv. to Py. II Obs., mg.	Calcd., mg.	Diff., mg.	Ratio[a] Py. I:Py. II
5.0	0.772	0.773	0.001	...	...	...	...
7.5	1.204	1.218	.014	0.988	1.017	0.029	1.22
12.5	2.041	1.972	− .069	1.639	1.645	.006	1.24
15.0	2.247	2.280	.033	1.968	1.943	− .025	1.14
17.5	2.489	2.543	.054	2.263	2.229	− .034	1.10
20.0	2.797	2.760	− .037	2.471	2.504	.033	1.13
Av.			− .0007			.0018	1.166

[a] Calculated from dextrose equivalent to given weight of pyrethrin I and pyrethrin II; theoretical ratio, 1.133 (374/330).

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[10] Allihn, *J. prakt. Chem.*, **22,** 46 (1880).

It was expected that the amounts of dextrose equivalent to a given weight of the two pyrethrins would be inversely proportional to the molecular weights of the pyrethrins. This is shown to be approximately the case in Table III. Direct colorimetric comparisons were made between equal weights of pyrethrin I and pyrethrin II. The colorimeter readings were almost directly proportional to the molecular weights of the pyrethrins; the ratio of the pyrethrin II readings to the pyrethrin I readings was 1.152, compared with the theoretical ratio 1.133.

By substituting different values for y in Equation I, the weights of pyrethrin I equivalent to amounts of dextrose from 0.750 to 2.875 mg. were calculated. These calculations were made at intervals of 0.125 mg. of dextrose and other values were interpolated at intervals of 0.025 mg. In this way Col. II of Table IV was formed.

TABLE IV

COPPER REDUCING POWER OF DEXTROSE AND PYRETHRINS[a]

Dextrose, mg.	Pyrethrin I, mg.	Pyrethrin I and II, mg.	Dextrose, mg.	Pyrethrin I, mg.	Pyrethrin I and II, mg.	Dextrose, mg.	Pyrethrin I, mg.	Pyrethrin I and II, mg.
0.750	4.87	5.19	1.475	9.07	9.68	2.200	14.31	15.26
.775	5.01	5.34	1.500	9.23	9.85	2.225	14.52	15.49
.800	5.14	5.48	1.525	9.39	10.02	2.250	14.73	15.71
.825	5.28	5.63	1.550	9.55	10.19	2.275	14.95	15.94
.850	5.41	5.77	1.575	9.72	10.37	2.300	15.17	16.18
.875	5.55	5.92	1.600	9.88	10.54	2.325	15.40	16.42
.900	5.69	6.07	1.625	10.04	10.71	2.350	15.62	16.66
.925	5.82	6.21	1.650	10.21	10.89	2.375	15.85	16.91
.950	5.96	6.36	1.675	10.38	11.07	2.400	16.09	17.16
.975	6.10	6.51	1.700	10.55	11.25	2.425	16.33	17.42
1.000	6.24	6.66	1.725	10.72	11.43	2.450	16.57	17.68
1.025	6.38	6.81	1.750	10.89	11.62	2.475	16.81	17.93
1.050	6.52	6.95	1.775	11.07	11.81	2.500	17.05	18.19
1.075	6.67	7.11	1.800	11.24	11.99	2.525	17.31	18.46
1.100	6.81	7.26	1.825	11.42	12.18	2.550	17.58	18.75
1.125	6.95	7.41	1.850	11.60	12.37	2.575	17.85	19.04
1.150	7.10	7.57	1.875	11.78	12.57	2.600	18.11	19.32
1.175	7.25	7.73	1.900	11.96	12.76	2.625	18.38	19.61
1.200	7.39	7.88	1.925	12.15	12.96	2.650	18.67	19.91
1.225	7.54	8.04	1.950	12.33	13.15	2.675	18.95	20.21
1.250	7.69	8.20	1.975	12.52	13.35	2.700	19.25	20.53
1.275	7.84	8.36	2.000	12.71	13.56	2.725	19.56	20.86
1.300	7.99	8.52	2.025	12.90	13.76	2.750	19.86	21.18
1.325	8.14	8.68	2.050	13.10	13.97	2.775	20.20	21.55
1.350	8.29	8.84	2.075	13.30	14.19	2.800	20.55	21.92
1.375	8.44	9.00	2.100	13.49	14.39	2.825	20.89	22.28
1.400	8.60	9.17	2.125	13.69	14.60	2.850	21.24	22.65
1.425	8.76	9.34	2.150	13.90	14.82	2.875	21.59	23.03
1.450	8.92	9.51	2.175	14.11	15.05			

[a] Third column calculated for a mixture of equal parts of pyrethrin I and II.

Staudinger and Ruzicka found that the active material, in the flowers they used, consisted of about 40% of pyrethrin I and 60% of pyrethrin II. The proportion of the two pyrethrins in the flowers probably varies.[2] It was assumed that the pyrethrins occur in equal amounts, and from the values for pyrethrin I, in Table IV, the corresponding values for a 1:1 mixture of pyrethrin I and II were calculated, using the average molecular weight *352* and multiplying the figures for pyrethrin I by the factor 1.06666 (third column, Table IV).

The semicarbazones of the pyrethrins had little or no copper reducing action. The by-products of the semicarbazone conversion, with oxalic acid, were carefully examined for copper reducing compounds; none was found that resisted the purification with sodium hydroxide, chromic acid and permanganate.

The pyrethrins were altered by prolonged beating at 90°; they became insoluble in petroleum ether and lost their activity but the copper reducing power was increased slightly. Saponification of pyrethrin I with alcoholic sodium hydroxide solution lowered the copper reducing power.

The semicarbazone of pyrethrolon was prepared from the mixed semicarbazones of pyrethrin I and II by saponification at 0°, with a methanol solution of sodium hydroxide.[11] The pyrethrolon semicarbazone melted at 203°; it was converted into the ketone-alcohol by prolonged shaking with benzene and potassium bisulfate solution.

The copper reducing power of pyrethrolon was slightly less than that of pyrethrin I. Pyrethrolon was dissolved in petroleum ether and washed with 3% potassium permanganate solution; 98.5% of the pyrethrolon was oxidized and removed from the petroleum ether. The residue from the evaporation of the petroleum ether solution had very little copper reducing action.

Application of the Copper Reduction Method to Pyrethrum Flowers.—Having found that the amount of pure pyrethrins in alcoholic solution could be determined accurately, it remained to apply the method to pyrethrum flowers and to eliminate, by appropriate means, any other copper reducing material that might be present.

Preliminary tests with petroleum ether extracts yielded percentages of pyrethrins of about the magnitude expected. Washing the petroleum ether extracts with 1% sodium hydroxide or with concentrated sodium bisulfite solution did not remove any material that reduced alkaline copper solution.

Staudinger and Ruzicka found that the pyrethrins in petroleum ether solution were not oxidized by chromic acid solution. Washing the petroleum ether extracts of *Pyrethrum* flowers with chromic acid solution did not decrease the amount of copper reducing material. No petroleum ether

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[11] Staudinger and Ruzicka, *cf.* ref. 4, pp. 196 and 216.

soluble compounds that reduced copper could be found, excepting the pyrethrins.

The residues from the purification of the semicarbazones of the pyrethrins were carefully examined for petroleum ether soluble copper reducing compounds but none was found.

No other compounds that formed semicarbazones could be isolated from the petroleum ether extract excepting the pyrethrins; this agrees with the findings of Staudinger and Ruzicka.

Application of the method to daisy flowers (*Chrysanthemum leucanthemum)* showed no pyrethrins present and tests on *Pyrethrum* stems yielded mere traces of pyrethrins. Finally, the pyrethrins were isolated from 2500 g. of *Pyrethrum* flowers and weighed as semicarbazones. The same flowers were analyzed by the copper reduction method; the gravimetric method yielded 0.66% of pyrethrins; the copper reduction method, 0.88%. In view of the unavoidable losses in separating the semicarbazones, the agreement is good.

It is believed, therefore, that the following method determines only the toxic principles in *Pyrethrum* flowers.

Method for the Evaluation of Pyrethrum Flowers

Reagents. (a) Petroleum ether, 90–99% distilling between 20 and 40"; maximum boiling point, 60°.

(b) Aldehyde-Free **Alcohol.**[12]—Allow 95% alcohol, containing 5 g. of *m*-phenylenediamine hydrochloride per liter, to stand for twenty-four hours with frequent shaking. Boil under a reflux condenser for at least eight hours, allow to stand overnight and distil, rejecting the first 10 and the last 5% of distillate. Store in a dark place in well-filled bottles.

(c) Basic Lead Acetate Solution.—Dissolve 20 g. of Horne's basic lead acetate in sufficient recently boiled water to make 1 liter.

(d) Alkaline Copper Solution.—Dissolve 2.5 g. of purest copper sulfate, $CuSO_4.5H_2O$, in about 100 cc. of water, warming gently; cool when dissolved. Dissolve 5 g. of highest purity sodium potassium tartrate and 7.5 g. of purest sodium hydroxide separately in about 100 cc. of cold water. Transfer the solutions to a 500-cc. volumetric flask, mix and dilute to the mark. This solution should not be used after it is three days old.

(e) **Folin's Reagent.**[13]—Dissolve 150 g. of sodium molybdate, $Na_2MoO_4{\cdot}2H_2O$, in 300 cc. of water. Filter through a 15-cm. quantitative filter paper into a 1-liter flask and wash with 75 cc. of water. Add 0.1 to 0.2 cc. of bromine and shake until the bromine is dissolved. Let stand for one hour, then add with shaking 225 cc. of 85% phosphoric acid. Add 150 cc. of sulfuric acid (1 vol. of concentrated acid mixed with 3 vols. of water and cooled). Remove the liberated bromine by means of a moderately rapid current of air; the aëration requires about half an hour. Finally add 75 cc. of 99% acetic acid, mix and dilute to a volume of 1 liter.

(f) Standard Dextrose Solution.—Dissolve exactly 1 g. of pure anhydrous dextrose

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[12] "Methods of Analysis," Association of Official Agricultural Chemists, Washington, D. C., **1925,** 2d. ed., p. 353.

[13] Folin, *J. Biol. Chem.*, **67,** 357–370 (1926).

in water and transfer to a 200-cc. volumetric flask. Add 40 cc. of aldehyde-freealcohol, mix and dilute to 200 cc. with water. Transfer 10 cc. of this solution to a 250-cc. volumetric flask by means of a pipet, add 210 cc. of aldehyde-free alcohol and dilute to 250 cc. with water. Ten cc. of this dilute solution contains 2 mg. of dextrose. The strong solution is stable for months; the dilute solution should be made fresh each week.

Apparatus. (a) Constant-temperature water bath, set at 78°, corrected, and controlled within ±0.2°.

(b) **Colorimeter** of Duboscq or Klett type, with artificial illuminator.

(c) Folin sugar **tubes,**[14] blown to contain 15.5 cc. to base of constriction. When heated to 78° the surface of the liquid must fall between points **A** and B, Fig. 1. The internal diameter of the constricted portion should be the same for all tubes in a set.

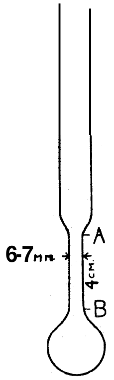

Fig. 1.—Modified Folin tube. Bulb contains 15.5 cc. to Point B.

Determination.—Extract 20 g. of ground *Pyrethrum* flowers (about 30-mesh) for five hours with petroleum ether in a Soxhlet extractor. Cool the petroleum ether solution to about 20" and let stand for at least half an hour. Filter through a quantitative filter paper into a 400-cc. beaker, add a few grains of ignited sand and evaporate at a temperature not exceeding 75°. As soon as the last traces of petroleum ether are driven off, transfer the residue with five or six portions of boiling 95% aldehyde-free alcohol to a 100-cc. volumetric flask (previously marked at the 80-cc. point), using sufficient boiling alcohol to make the volume 80–85 cc. To the hot solution add from a pipet 15 cc. of basic lead acetate solution and make to the mark with hot alcohol. Shake vigorously, cool at once to 20° and again make to the mark with alcohol. Filter and to the filtrate add about 1 g. of anhydrous sodium carbonate. Let stand for ten to fifteen minutes, shaking frequently, and filter. Immediately pipet 10 cc. of the clear filtrate into a Folin tube and add, also from a pipet, 6 cc. of alkaline copper solution. Mix thoroughly, keeping the solution in the bulb of the tube. Measure 10 cc. of standard dextrose solution (2 mg. of dextrose) with a pipet into *a* second tube and add 6 cc. of copper solution. Place the tubes upright in the constant-temperature bath, set at 78° corrected, and heat for exactly forty-five minutes. Remove from the bath and place in water at 20° for three minutes. Add 10 cc. of Folin's reagent from a pipet and let stand for three minutes; then stopper the tubes, mix thoroughly, transfer to 100 cc. volumetric flasks and make to the mark with water. Filter through a Gooch crucible fitted with a heavy asbestos pad, using gentle suction. Do not use filter paper. The dextrose solution need not be filtered. Compare the solutions at once in the colorimeter and from the readings calculate the dextrose equivalent to the unknown solution in the usual way. Reference to Col. **3** of Table IV will give the amount of pyrethrins, in milligrams, equivalent to the dextrose found in the unknown solution, or milligrams of pyrethrins in the 2 g. aliquot of flowers taken.

Discussion of Method

Blank determinations were run several times each day, or with nearly every set of tests. No difficulty was experienced in obtaining blanks equivalent to 0.05 mg. of dextrose, and for this reason no correction for the blank was made in calculating Table IV. Reagents that yield a blank equivalent to more than 0.10 mg. of dextrose should be rejected. High blanks may be due to impurities in any of the reagents, but the sodium potassium tartrate,

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[14] Folin, J. *Biol. Chem.*, ***41,*** 372 (1920).

sodium molybdate and aldehyde-free alcohol especially should be carefully tested. If the blank is between 0.05 and 0.10 mg. of dextrose, when compared with the standard dextrose solution, the error due to the blank is negligible.

The petroleum ether extract should not be heated longer than necessary to drive off the solvent. Generally only five or ten minutes' heating above 60° will be required if the petroleum ether meets the specifications given. High-boiling petroleum ether should not be used.

The proportion of alcohol and water in the contents of the Folin tubes is carefully adjusted; if more alcohol is used the copper salts will be precipitated; if the percentage of water is increased the pyrethrins will be thrown out of solution. In either case incorrect results will be obtained. The Folin tubes should be dried before using and the measurements should be made with pipets. Smaller aliquots than 10 cc. can be used for a determination, but sufficient aldehyde-free alcohol (80.5%) must be added to the tube to make the total volume of the pyrethrin solution 10 cc. Larger aliquots than 10 cc. cannot be used.

It is essential that the bath be maintained at 78° corrected, ±0.2°, and a stirrer should be provided to insure even temperature and circulation around the tubes, which should be immersed to a depth of 8 to 10 cm. Variations in time of heating or in temperature will yield results that are not comparable with Table IV. After removing the tubes from the bath they should be treated as nearly alike as possible; therefore it is inadvisable to run more than 3 or 4 tubes at a time.

In making the color comparisons the standard dextrose is set at 20 mm. The unknown will then read between 14 and 50 mm., for quantities between 23 and 5 mg. of pyrethrins. If the reading is less than 12 mm., the entire amount of copper may have been reduced, and the determination should be repeated using a smaller aliquot. It is also desirable, if the reading is more than 40 mm., to run a duplicate determination using 40 g. of flowers instead of 20.

The pyrethrins, in petroleum ether solution, can be washed with dilute sodium hydroxide solution, concentrated sodium bisulfite solution and 3% chromic acid solution without appreciable loss. These methods of purification were not necessary for the analysis of the flowers, but may be used in the examination of *Pyrethrum* sprays.

The dextrose used as standard in this work was of the highest purity obtainable and was dried for thirty days over sulfuric acid. All volumetric glassware, weights and thermometers used were Bureau of Standards certified. Colorimeter readings were made with artificial light and a blue glass screen.

Percentage of Toxic Principles in Pyrethrum Flowers.—The foregoing method was applied to *Pyrethrum* flowers and stems and to daisy flowers. The analyses are shown in Table V.

TABLE V

DETERMINATION OF PYRETHRIN CONTENT OF FLOWERS AND STEMS

No.	Description of sample	Pyrethrins %	No.	Description of sample	Pyrethrins, %
7	Pyrethrum flowers, 1928 crop	0.40	2	Pyrethrum flowers, 1926 crop	0.87
6	Pyrethrum flowers, 1927 crop	.43	20	Pyrethrum flowers, 1928 crop	.94
13	Pyrethrum flowers, 1925 crop	.44	19	Pyrethrum flowers, 1928 crop	1.10
21	Pyrethrum flowers, 1925 crop	.45	17	Pyrethrum flowers, 1928 crop	1.17
16	Pyrethrum flowers, 1925 crop	.47	18	Pyrethrum flowers, 1928 crop	1.20
14	Pyrethrum flowers, 1925 crop	.53	1	Pyrethrum flowers, 1928 crop	1.21
4	Pyrethrum flowers, 1927 crop	.56	8	Dalmatian stems, 6 years old	0.00
11	Pyrethrum flowers, 1925 crop	.57	9	Spanish stems, 1927 crop	.04
5	Pyrethrum flowers	.59	15	Dalmatian stems	.04
3	Pyrethrum flowers, 1928 crop	.80	22	Daisy flowers, 3 years old	.00

The pyrethrin content varied, in the samples examined, from 0.40 to 1.21%; duplicate determinations agreed within 0.03% or less. The range of the pyrethrin content found is greater than reported by Staudinger and Harder (0.4 to 0.6%); Staudinger and Ruzicka found only 0.3% of pyrethrins in the flowers they examined.

Further work is in progress to determine the comparative value of the different varieties and grades of *Pyrethrum,* and to determine the distribution of the active principles in the different parts of the flower. The method is also being adapted to the examination of oleo-resin of *Pyrethrum* and to the analysis of *Pyrethrum* insecticidal sprays for household and garden use.

Summary

1. Pyrethrin I and II have been isolated from Japanese *Pyrethrum* flowers, and their action on alkaline copper solution has been investigated. The copper reducing power of the pyrethrins has been compared with that of dextrose.
2. A method has been described for determining the percentage of active principles in *Pyrethrum* flowers.
3. The percentage of pyrethrins ranged from 0.40 to 1.21%, in the sixteen samples of *Pyrethrum* flowers examined.
4. *Pyrethrum* stems contain about one-tenth the amount of pyrethrins found in the poorest flowers.
5. Daisy flowers contain no pyrethrins.
6. The active principles of Japanese *Pyrethrum* are the same as those of Dalmatian *Pyrethrum* flowers.
7. The toxicity of the pyrethrins to cockroaches has been determined.

MINNEAPOLIS, MINNESOTA

[Contribution from the Chemical Laboratory of Hobart College]

A SERIES ARRANGEMENT OF ORGANIC GROUPS. I. AS DETERMINED BY THE HALOGENATION OF MIXED STANNANES

By Ralph H. Bullard

Received May 14, 1929 Published October 5, 1929

When a tetra-alkyl- or arylstannane is treated with two atoms of halogen one of the organic groups is replaced by halogen. The reaction is represented by the equation $R_4Sn + X_2 = R_3SnX + RX$. When a mixed alkyl- or alkylarylstannane such as R_3SnR' is halogenated, two reactions are possible

$$R_3SnR' + X_2 = R_3SnX + R'X \quad (1)$$
$$R_3SnR' + X_2 = R_2R'SnX + RX \quad (2)$$

It is a remarkable fact that in general only one of these reactions occurs. We may consider, therefore, that the velocity of one reaction is enormously greater than that of the other, or that the affinities of the groups are such that only one reaction occurs. In any case, the groups can be arranged in a series corresponding with the order of their removal by means of halogen.

Grüttner and Krause[1] from their investigations of mixed alkylplumbanes formulated a rule stating that, on bromination, the lightest group splits off first. Later, on working with mixed alkylstannanes, these authors state[2] that, without exception, the same rule applies to the alkylstannanes.

Frankland[3] and also Morganoff[4] state that, on iodination of dimethyldiethylstannane, $(CH_3)_2(C_2H_5)_2Sn$, the methyl group is removed before the ethyl. Pope and Peachey[5] found that on iodinating trimethylethylstannane, $(CH_3)_3C_2H_5Sn$, and dimethylethylpropylstannane, $(CH_3)_2(C_2H_5)(C_3H_7)Sn$, the methyl group is in each case removed first. Cahours,[6] however, reports that an ethyl group is removed on iodinating trimethylethylstannane. Bullard and Vingee[7] found that trimethylethylstannane, on bromination, yields dimethylethylstannyl bromide, $(CH_3)_2(C_2H_5)SnBr$, with the removal of a methyl group. This does not agree with the observations of Cahours but is in accord with those of Frankland, Morganoff and Pope and Peachey.

Ladenburg[8] found that iodination of triethylphenylstannane, $(C_2H_5)_3(C_6H_5)Sn$, yields iodobenzene and triethylstannyl iodide, $(C_2H_5)_3SnI$, while

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[1] Grüttner and Krause, *Ber.*, 50, 202 (1917).

[2] Gruttner and Krause, *ibid.*, 50, 1802 (1917).

[3] Frankland, *Ann.*, 111, 44 (1859).

[4] Morganoff, *ibid.*, 144, 157 (1867).

[5] Pope and Peachey, *Proc. Chem. Soc.*, 16, 42 (1900).

[6] Cahours, *Ann.*, 122, 49 (1862).

[7] Bullard and Vingee, This Journal, 51, 892 (1929).

[8] Ladenburg, (a) *Ber.*, 4, 17 (1871); (b) *Ann.*, 159, 251 (1871).

Krause and Schmitz[9] showed that the phenyl group is removed before ethyl with such reagents as silver nitrate or mercuric chloride. Bullard and Robinson[10] found that on bromination of trimethylphenylstannane, $(CH_3)_3(C_6H_5)Sn$, the phenyl group is removed.

It has been shown by Kipping and Smith[11] that the benzyl group is removed before ethyl by iodine, sulfuric acid or chlorosulfuric acid. Kraus and Bullard[12] showed that the benzyl group is removed on brominating trimethylbenzylstannane, $(CH_3)_3(C_6H_5CH_2)Sn$.

In the experimental part of this paper it is shown that the phenyl group is removed before the benzyl group.

From the above it is seen that the series of groups arranged in the order of decreasing ease of removal from tin by free halogen is as follows: phenyl, benzyl, methyl, ethyl, propyl.

In a later paper the author hopes to present the'order of substitution for mixed stannanes of the type $R_2SnR'_2$ when treated with halogen acids.

Experimental Part

Preparation of Triphenylbenzylstannane, $(C_6H_5)_3(C_6H_5CH_2)Sn$.—Triphenylstannyl iodide was dissolved in liquid ammonia and converted into the sodium salt by adding two atoms of sodium per mole of iodide. The theoretical amount of benzyl chloride was then added. A white precipitate was formed. The reaction took place according to the equation $NaSn(C_6H_5)_3 + C_6H_5CH_2Cl = (C_6H_5)_3(C_6H_5CH_2)Sn + NaCl$. The ammonia was allowed to evaporate and water was added to dissolve the sodium chloride. The residual white powder was dried and crystallized from petroleum ether; yield, practically quantitative. The substance melted at 90–91°.

Anal. Subs., 0.2579, 0.2584: SnO_2, 0.0873, 0.0880. Calcd. for $(C_6H_5)_3(C_6H_5CH_2)$-Sn: Sn, 26.94. Found: Sn, 26.66, 26.82.

Mol. wt. Subs., 0.3095, 0.4317: C_6H_6, 19.25, 19.25; *At,* 0.189, 0.267. Calcd. for $(C_6H_5)_3(C_6H_5CH_2)Sn$: mol. wt., 440.7. Found: mol. wt., 435.7, 426.8.

Bromination of Triphenylbenzylstannane.—The stannane was brominated by adding to its benzene solution cooled in ice water a carbon tetrachloride solution of four atoms of bromine per mole of stannane. Bromination took place instantly. The benzene and carbon tetrachloride were removed by distillation from a steam-bath under atmospheric pressure. The pressure was then reduced and a liquid was obtained which boiled under atmospheric pressure at 154° uncorr. This indicated the presence of bromobanzene. The residual liquid did not distil at 100° under a pressure of three millimeters. On cooling it solidified and was crystallized from petroleum ether. Large colorless prisms melting at 74–75' were obtained. This further indicated that phenyl groups had been removed with the formation of phenylbenzylstannyl dibromide because diphenylstannyl dibromide melts at 36–38'.

Anal. Subs., 0.1024, 0.1581: SnO_2, 0.0408, 0.0536. Calcd. for $(C_6H_5)(C_6H_5CH_2)$-$SnBr_2$: Sn, 26.59. Found: Sn, 26.69, 26.70. Subs., 0.1669, 0.2503: AgBr, 0.1391, 0.2099. Calcd. for $(C_6H_5)(C_6H_5CH_2)SnBr_2$: Br, 35.79. Found: Br, 35.47, 35.69.

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[9] Krause and Schmitz, Ber., 52, 2150 (1919).

[10] Bullard and Robinson, THIS JOURNAL, **49,** 1372 (1927).

[11] Kipping and Smith, *J. Chem. Soc.,* ***101,*** 2552 (1912).

[12] Kraus and Bullard, THIS JOURNAL, **48,** 2135 (1926).

Hence the bromination of triphenylbenzylstannane results in the removal of phenyl groups, the reaction proceeding according to the equation $(C_6H_5)_3$-$(C_6H_5CH_2)Sn + 2Br_2 = (C_6H_5)(C_6H_5CH_2)SnBr_2 + 2C_6H_5Br$.

The author wishes to acknowledge his indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant which assisted in defraying the expenses of the present investigation.

Summary

1. It has been shown that on bromination of triphenylbenzylstannane the phenyl groups are first removed.

2. The series arrangement of some organic groups based on the relative ease of removal from tin by halogen is: phenyl, benzyl, methyl, ethyl, propyl.

GENEVA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE CONSTITUTION OF TRIPHENYLSILICANE AND ITS REACTION WITH SODIUM IN LIQUID AMMONIA[1]

BY HARRY H. REYNOLDS,[2] LUCIUS A. BIGELOW AND CHARLES A. KRAUS

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The present study was undertaken as a part of a broader investigation now in progress in this Laboratory, which deals with certain of the fundamental properties of the element silicon in its organic combinations. In attacking this problem it was necessary to form organic silicon derivatives of the general type R_3SiNa to be used as reagents. Since the corresponding halides R_3SiX are completely ammonolyzed by liquid ammonia, it was attempted to prepare the desired compound by the action of sodium on triphenylsilicane in the same solvent. The corresponding reaction of sodium with triphenylstannane takes place readily and quantitatively. When, however, this simple reaction was attempted in the case of the silicane, unexpected results were obtained and it was found necessary to carry out a detailed study, the results of which are described in the present paper.

Ladenburg[3] reports the preparation of triphenylsilicane, melting at 200–203°, by the action of sodium and a little benzene upon triphenyl silicon bromide. On the face of it, this reaction seems a little improbable, especially in view of the fact that the corresponding triphenylstannane, and triphenylgermane, recently prepared, have been found to melt at

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[1] This paper is constructed from a portion of the Dissertation presented by Harry H. Reynolds to the Faculty of the Graduate School of Brown University, in June, 1928, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Rice Fellow, 1925–1926; Metcalf Fellow, 1926–1927.

[3] Ladenburg *Ber.*, 40, 2278 (1907).

about 25°[4] and 47°,[5] respectively. Our work has shown that the earlier results of Ladenburg are in error, and that the compound of the formula $(C_6H_5)_3SiH$ melts at 36°.[6]

The silicane, which is a white crystalline solid, was first synthesized by Nelson,[7] who treated silicochloroform with phenylmagnesium bromide. The reaction takes place according to the equation $SiHCl_3 + 3C_6H_5MgBr \longrightarrow SiH(C_6H_5)_3 + 3MgBrCl$. He analyzed the silicane for silicon but did not examine it further. The present writers have confirmed the synthesis and fully established the constitution of the compound in the following manner. (1) The molecular weight of the material was determined and found to correspond to the formula requirements; (2) the substance was quantitatively brominated and one mole of hydrogen bromide was evolved for each mole of the silicane used, and (3) the triphenyl silicon bromide formed in (2) yielded, upon hydrolysis, an approximately quantitative amount of pure, known triphenylsilicol, $(C_6H_5)_3SiOH$.

When triphenylsilicane is treated with sodium in liquid ammonia solution, a very simple reaction might be expected to take place, namely, $(C_6H_5)_3SiH + Na \longrightarrow (C_6H_5)_3SiNa + {}^1/_2 H_2$, which calls for the utilization of 1 gram atom of sodium and the evolution of $^1/_2$ mole of hydrogen per mole of the silicane employed. Actually, however, only $^2/_3$ gram-atom of sodium was consumed and 1.9 atoms of hydrogen were evolved in the reaction. Furthermore, since a distinct end-point was reached, the excess of hydrogen could not have come from any interaction between the sodium and the ammonia. If the above reaction occurred, the addition of ammonium bromide to the solution should regenerate the original material, according to the equation $(C_6H_5)_3SiNa + NH_4Br \longrightarrow (C_6H_5)_3SiH + NaBr + NH_3$. Actually, the product obtained under these conditions, upon evaporation of the liquid ammonia, consisted of a white crystalline solid melting at 175° and a thick sirup which was not further investigated. About two-thirds of the original silicon was recovered as crystalline solid. The addition of reagents other than ammonium bromide, such as ethyl or phenyl bromide or oxygen, yielded, in every case, the same crystalline product.

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[4] L. S. Foster, "Thesis," Clark University, **1923.**

[5] Kraus and Foster, THIS JOURNAL, **49,** 465 (1927).

[6] Since the above was written an article has appeared by Kipping and Murray, *J. Chem. Soc.*, **131, 360** (1929), in which they have prepared a substance believed to be triphenylsilicane, as a by-product in the destructive distillation of octaphenylcyclosilicotetrane under reduced pressure. They describe it as an oil which did not solidify at 0°. Analyses, molecular weight determination and hydrogen equivalent, corresponding closely to the values required by the formula $(C_6H_5)_3SiH$ are given, as well as certain reactions tending to confirm the constitution of the product. It seems certain that these investigators had in hand a somewhat impure sample of the silicane, as it failed to solidify at 0°.

[7] Walter K. Nelson, unpublished work, **1927.**

The substance melting at 175° is very stable, not being affected by the air or even by boiling dilute sodium hydroxide. It is rather difficultly soluble in alcohol and crystallizes well from this solvent. When analyzed for silicon it gave figures closely corresponding to the values required for triphenylsilicon or hexaphenylsilico-ethane, while molecular weight determinations yielded values closely approximating those required by the formula $[(C_6H_5)_3Si]_2$ or hexaphenylsilico-ethane. However, this latter compound has previously been synthesized and melts at 354°.[8] We have prepared a sample of this silico-ethane by the method described in the literature and have shown that our substance is structurally different, inasmuch as no transition from one into the other occurred when they were melted together.

The material melting at 175° was brominated in carbon tetrachloride in an effort to throw light upon its constitution. One-half of the silicon appeared as triphenyl silicon bromide, while all the rest of the bromine employed went to form bromobenzene. A very small quantity of di-triphenyl silicon oxide was also isolated. The remainder of the material produced in the bromination consisted of pasty by-products which were not further examined. No definite conclusions could be drawn from these experiments.

At this point it was discovered that the substance melting at 175° could be hydrolyzed readily by means of hydrochloric acid, and that the inorganic product of hydrolysis was ammonium chloride. Inasmuch as our material was quantitatively stable toward boiling alkali, and since all compounds containing a silicon–nitrogen linkage, with which we were familiar, hydrolyzed even in moist air, this observation was entirely unexpected. However, it was established that the material contained 2.6% of nitrogen, which corresponds closely to that required by di-triphenylsilicon-imine, $[(C_6H_5)_3Si]_2NH$. The analytical results above described correspond, within the normal limits of error, to the values required by this formula, while the amount of hydrogen evolved in the preparation, as well as the phenomena observed in the bromination, may also be accounted for. Finally, the product of hydrolysis of the imine, other than ammonium chloride, which should be triphenylsilicol, has been identified as such.

A somewhat similar reaction has been observed in this Laboratory by Eatough,[9] who treated triphenylsilicane with lithium dissolved in ethyl amine. In this case, also, $^2/_3$ gram-atom of the metal reacted with 1 mole of the silicane and 1 mole of hydrogen was evolved, but the products were not further investigated. The mechanism of these reactions is as yet obscure, though undoubtedly complex.

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[8] Schlenk, Renning and Racky, *Ber.*, 44, 1178 (1911).

[9] Harry Eatough, unpublished work, 1928.

Altogether, the structure of the substance melting **at** 175" seems definitely established as di-triphenylsilicon-imine, notwithstanding its extraordinary stability in alkaline solution, not frequently observed in compounds of this type.

Experimental

Triphenylsilicane.—This compound was prepared according to the method of Nelson[7] as follows. A Grignard reagent was prepared in the usual manner from 185 g. of bromobenzene, 28.6 g. of magnesium and 400 cc. of anhydrous ether. This solution (4.5 molar equivalents) was cooled to 0° and 36.2 g. of silicochloroform dissolved in 200 cc. of anhydrous ether was slowly added to it. After standing at room temperature for two hours the mixture was boiled for twenty hours. The resulting crystalline mass was cooled to 0°, acidified with dilute sulfuric acid, extracted with ether and the solvent distilled. The residue was fractionated twice at 2 mm. and the final product collected from 152–167°. It condensed as a colorless oil which on cooling solidified to a white solid; yield, 52 g. or 73% of the theoretical. Upon recrystallization from 95% alcohol, under 21°, white plates were formed melting at 36–37°. At higher temperatures the compound separated as an oil.

Anal. (Nelson) Subs., 0.3716, 0.3580, 0.4880: SiO_2, 0.0852, 0.0830, 0.1131. Calcd. for $C_{18}H_{16}Si$: Si, 10.78. Found: Si, 10.71, 10.83, 10.83.

Mol. wt. Subs., 0.1941, 0.1930, 0.1941: Benzene, 21.79, 21.77, 21.77; AT, 0.177°, 0.173°, 0.179°. Calcd. for $C_{18}H_{16}Si$: 260. Found: 252, 256, 249.

Bromination of Triphenylsilicane in Carbon Tetrachloride Solution.—In this experiment an all glass apparatus was used, arranged in such a manner that a current of nitrogen could be passed through the reacting mixture and the gases produced (N_2, HBr and CCl_4 vapor) conducted through a reflux condenser and then an absorption train. This consisted of a trap containing metallic mercury to absorb free bromine, a U-tube immersed in liquid ammonia to condense any carbon tetrachloride vapor and finally a series of bulbs partly filled with 10% sodium hydroxide solution to absorb all the hydrobromic acid evolved. One mole of triphenylsilicane was placed in this apparatus and 1 mole of bromine dissolved in carbon tetrachloride added through a side tube. The mixture was allowed to stand for some time to complete the reaction and the carbon tetrachloride was then frozen by means of a liquid ammonia bath to liberate the dissolved hydrobromic acid. A current of dry nitrogen was now passed through the solidified mass to carry all the hydrobromic acid into the absorption train. In the course of an hour the mixture was allowed to warm up and was finally boiled to expel the last traces of hydrobromic acid. The sodium hydroxide solution was carefully washed out of the bulbs, acidified with nitric acid and the bromine precipitated as silver bromide in the usual manner.

Anal. Subs., 1.000: Br, 0.614; AgBr, 0.724. Mols HBr/mole subs.: 1.00.

Upon hydrolysis of the brominated product formed in the reaction by boiling with dilute sodium hydroxide solution, a 93% yield of practically pure triphenylsilicol (m. p. 148–151°) was obtained.

Reaction between Triphenylsilicane and Sodium in Liquid Ammonia.—To a suspension of triphenylsilicane in anhydrous ammonia there was added, in small portions, one mole of metallic sodium. As the metal was added, a moderately vigorous reaction occurred, accompanied by the appearance of a deep red color and the copious evolution of an inflammable gas, later identified as hydrogen. As the reaction progressed the silicane gradually dissolved and a colorless crystalline product separated. When approximately two-thirds of the sodium had been added, the evolution of gas ceased and a permanent blue color, due to **an** excess of the metal, was imparted to the solution. Further additions of sodium produced no further apparent change. Ammonium bromide was then added, in small portions, to the mixture. The blue color was first discharged and the red color gradually faded, with the momentary formation of a white curdy precipitate. The color finally disappeared entirely, and from then on until one mole of ammonium bromide had been added, a white curdy precipitate continued to be formed. When the reaction was complete, the liquid ammonia was allowed to evaporate and the reaction mixture was extracted with carbon tetrachloride. The solvent was removed by distillation and a white solid mass remained which, upon recrystallization from 95% alcohol, yielded a white crystalline product melting at 170–175°. Approximately two-thirds of the product consisted of this substance and the remainder, recovered by evaporating the alcoholic mother liquor, was a thick sirup, from which no single substance could be isolated. Further crystallization of the solid from alcohol yielded long white needles melting at 175°.

It was especially noteworthy, in the above reaction, that the addition of ethyl bromide, phenyl bromide or oxygen, instead of ammonium bromide, yielded in every case the same crystalline product, m. p. 175°. This indicated that the substance was formed directly by the action of the sodium with the triphenylsilicane, and not later upon the addition of ammonium bromide.

Anal. Subs., 0.3008, 0.3002, 0.3901: SiO_2, 0.0683, 0.0692, 0.0896. Subs., 0.3808, 0.5101: 16.58, 14.39 cc. of 0.1008 N NaOH; 20.04, 20.18 cc. of 0.1199 N HCl; blank, 0.23 cc. of HCI. Calcd. for $C_{36}H_{31}Si_2N$: Si, 10.61; N, 2.62. Found: Si, 10.66, 10.82, 10.78; N, 2.59, 2.58.

Mol. wt. Subs., 0.3866, 0.3807: benzene, 21.78, 21.78; AT, 0.174°, 0.167°. Calcd. for $C_{36}H_{31}Si_2N$: 534. Found: 510,524.

The analysis for silicon was carried out by treating the sample in a pyrex test-tube with fuming sulfuric acid and then with successive portions of fuming nitric acid until decomposition was complete. The acids were evaporated and the residue of silicon dioxide was ignited and weighed.

The analysis for nitrogen was conducted in the following manner. The sample was boiled for half an hour with 6 N hydrochloric acid, the mixture filtered and the residue washed free from chlorides. The filtrate was evaporated to a small volume, poured into a Kjeldahl apparatus, made alkaline and the ammonia collected in the usual manner in standard hydrochloric acid. The residue from the filtration, on crystallization from petroleum ether, melted at 151–152°. A known sample of triphenylsilicol, $(C_6H_5)_3SiOH$, and a mixture of the two each melted at the same point.

Quantitative Determination of the Gas Evolved in the Reaction between **Triphenylsilicane** and Sodium in Liquid Ammonia.—The treatment of the silicane with the sodium was carried out in an apparatus arranged in such a manner that all of the gas evolved might be collected over water, to dissolve most of the ammonia. The gas was then drawn very slowly through a drying tube containing phosphorus pentoxide into an evacuated bulb of known weight and volume. A manometer was attached to the system and the volume of the drying tube and connecting tubes was known. The molecular weight of the gas was calculated from the weight, pressure and temperature of the gas in the density bulb, together with the known volume of the bulb. The total volume of the gas at N.T.Y. was determined in a similar manner from its pressure, temperature and the known volume of the entire containing system. The molecular weight obtained indicated that the gas must be hydrogen, and a correction to the total volume of hydrogen was calculated, upon the assumption that the only impurity in it was ammonia. The results of this experiment are indicated below.

Mol. *wt.* Gas in bulb, 0.0115, 0.0156 g.; P, 200, 212 mm.; *T*, 25°, 27"; vol. of

bulb, 351.4 cc. Calcd. for H_2: 2.0. Found: 3.1, 3.9. ***Total vol. of gas.*** **Subs., 1.086, 1.029; Na, 0.096, 0.091; P, 200, 212 mm.; T, 25°, 27°; vol. of system, 391 cc.; vol. of pure H at N.T.P., corr. for NH_3 content, 87.0, 86.4 cc. Gram atoms of H_2 per mole of $(C_6H_5)_3SiH$, 1.8, 1.9.**

Summary

1. The constitution of triphenylsilicane, melting at 36°, has been established.
2. The reaction between triphenylsilicane and sodium in liquid ammonia has been studied. The chief product of the reaction was found to be di-triphenylsilicon-imine, $[(C_6H_5)_3Si]_2NH$.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE DENVER STATION, FOOD, DRUG AND INSECTICIDE ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

MONOBROMOGUAIACOL CARBONATE. ESTIMATION OF GUAIACOL CARBONATE

BY LEWIS H. CHERNOFF

RECEIVED MAY 1, 1929 PUBLISHED OCTOBER 5, 1929

As far as the writer is aware there are only two published methods for the estimation of guaiacol carbonate. One method[1] depends on the solubility of the carbonate in ether and its use is therefore limited to mixtures which do not contain other ether-soluble substances. In the other[2] the substance is saponified with alcoholic potassium hydroxide, acidified and after the addition of sodium chloride the volume of guaiacol is read.

The method herein described is more specific and depends on the conversion of guaiacol carbonate into a bromine derivative insoluble in 50% methyl alcohol.

When bromine is added to a solution of guaiacol carbonate in methyl alcohol, large needle-like crystals begin to separate out almost immediately. The compound is reasonably pure and after recrystallization from hot 95% ethyl alcohol melts sharply to an oil at 178°. It is easily soluble in chloroform, ether, benzene and hot methyl and ethyl alcohols, but less easily soluble in the cold alcohols. In water and petroleum ether it is insoluble.

A bromine determination by the Pringsheim method[3] slightly modified indicates the compound to be a monobromo guaiacol carbonate. This is apparently a new compound, as it does not seem to be described in the literature.

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[1] Abstracted in *Quart. J. Pharm.*, 1, 432 (1928); *Apoth. Ztg.*, 43, 198 (1928).

[2] A. Fernan, *Z. Oesterr. Apoth. Vr.*, 49, 165 (1911); *C. A.*, 5, 3324 (1911).

[3] Scott, "Standard Methods of Analysis," D. Van Nostrand Co., Inc., New York, 1917, 2d ed., revised, p. 122; *Chem. News*, 91, 215, 2372 (1905). The mixture of substance with sodium peroxide was heated slowly in a nickel crucible until melted. The contents was then allowed to cool and the whole plunged into water.

Anal. Subs., 0.2 g.: AgBr, 0.1763. Calcd. for $(BrC_6H_3OCH_3)_2O_2CO$: Br, 37.07. Found: Br, 37.50.

Method

To 0.1–0.5 g. of guaiacol carbonate in a 100-cc. Erlenmeyer flask add 10–20 cc. of methyl alcohol. Heat on the steam-bath until all of the substance is dissolved. Remove from the bath while hot, add about 1 cc. of bromine and let stand for ten minutes, shaking occasionally to promote crystallization. Add an equal volume of water and allow to stand for ten minutes longer. Filter through asbestos in a weighed Gooch crucible, wash with 50% methyl alcohol, dry for about an hour at the temperature of boiling water and weigh. Multiply the weight of the bromine derivative by the conversion factor 0.6343 to obtain the weight of guaiacol carbonate.

The bromine derivative is somewhat soluble in methyl alcohol and the addition of water is necessary to precipitate it completely. The following table shows the results obtained with pure guaiacol carbonate.

TABLE I

RESULTS WITH PURE GUAIACOL CARBONATE

Subs., g.	Bromine deriv., g.	Equiv. guaiacol carbonate, g.	Error, %
0.5	0.7788	0.4939	1.2
.1	.1567	.0994	0.6
.1	.1575	.0999	.1
.01	.0158	.0100	.0

When only one-fourth volume of water is added, the error becomes slightly larger, as is shown in Table II.

TABLE II

ERROR WITH LESS WATER

Subs, g.	Bromine deriv., g.	Equiv. guaiacol carbonate, g.	Error, %
0.5	0.7586	0.4812	3.8
.1	.1533	.0972	2.8
.1	.1557	.0988	1.2

Mixtures

In mixtures with the usual excipients such as starch, sugar and the gums acacia and tragacanth, a preliminary separation by the use of proper solvents may be made. Chloroform, in which the carbonate is easily soluble, is useful.

Mix 0.5 to 0.1 g. of powdered material with 10 cc. of chloroform, heat to boiling and filter through a small paper into an evaporating dish. Wash thoroughly with chloroform and evaporate the solution on the steam-bath. Dissolve the residue in hot methyl alcohol and brominate as above.

The results shown in Table III were obtained on three different mixtures whose compositions were unknown to the writer at the time of analysis. Later their compositions were given for comparison,

TABLE III

RESULTS ON UNKNOWN MIXTURES

Mixture	Composition, %	Guaiacol carbonate found, %
1	Guaiacol carbonate, 31.5; sucrose, 0.5; starch, 68.0	29.38, 30.64
2	Guaiacol carbonate, 51.5; sucrose, 9.5; acacia, 1.0; starch, 38.0	49.16, 49.76
3	Guaiacol carbonate, 63.7; tragacanth, 0.3; starch, 36.0	63.5, 63.89

A sample of commercial 5-grain guaiacol carbonate tablets was prepared by pulverizing twenty tablets, the average weight of each being 0.3865 g. or 5.96 grains. Three-tenths gram samples were analyzed according to the method for mixtures, with the check results 75.53 and 75.56%. The average content, therefore, was 4.50 grains instead of the declared 5 grains.

Summary

A new method for the estimation of guaiacol carbonate, depending on the conversion of guaiacol carbonate into a monobromo derivative, and a new compound, monobromo guaiacol carbonate, are described.

Acknowledgement is made to L. E. Warren of the Food, Drug and Insecticide Administration for submitting the problem and furnishing the "unknowns."

DENVER, COLORADO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

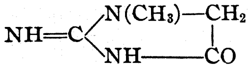
NEW DERIVATIVES OF CREATININE AND DIKETOPIPERAZINE[1,2]

BY L. R. RICHARDSON AND CLAUDE E. WELCH WITH S. CALVERT

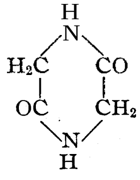
RECEIVED MAY 25, 1929 PUBLISHED OCTOBER 5, 1929

Creatinine, since it is excreted by the animal body, and diketopiperazine, because recent research has indicated that it is an integral part of the protein molecule, are both of great physiological importance. Extensive investigations of the physiological nature of creatinine have been completed but the known chemical reactions of both compounds are comparatively few in number.

A consideration of the formulas of these substances shows that both contain methylene groups



Creatinine



Diketopiperazine (keto form)

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[1] An abstract of the theses submitted by L. R. Richardson and Claude E. Welch in partial fulfilment of the requirements for the degree of Master of Arts in Chemistry at the University of Missouri.

[2] Revised paper; original manuscript received August 6, 1928.

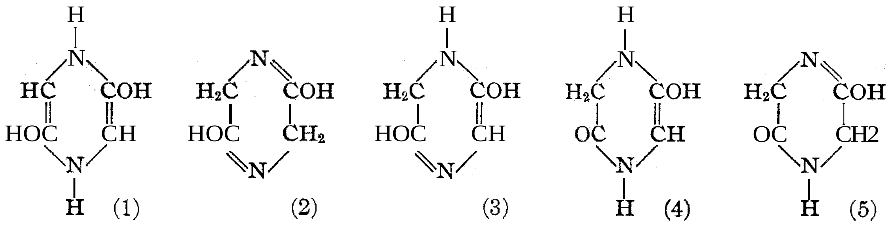
Methylene groups, if sufficiently affected by one or more negative groups such as the carbonyl group, tend to react with aldehydes,[3] substituted amidines and at times with an anilide such as benzylidene aniline. It seemed not unreasonable that similar condensations might be expected with creatinine and diketopiperazine.

Efforts to condense diphenylformamidine with creatinine were successful. We have not yet, however, succeeded in determining the precise formula of the product obtained. This work is being continued.

It was found that aldehydes condense very easily with creatinine upon fusion. Several aromatic aldehydes were condensed in this manner. The derivative that was prepared with benzaldehyde was prepared by Greenwald from creatine[4] and, during the course of these experiments, by Nicolet and Campbell[5] from the dihydrochloride of 5-benzalcreatinine. We have prepared this compound by two different methods: by fusing creatinine with benzaldehyde and with benzylidene aniline. Creatinine was condensed with vanillin and m-nitrobenzaldehydein the same manner.

Diketopiperazine, however, fails to condense with aromatic aldehydes on fusion. It seems that the only suitable method of effecting condensation is an application of the Perkin synthesis first applied to diketopiperazine by Sasaki:[6] several hours' heating of a mixture of the parent compounds in the presence of sodium acetate and acetic anhydride. 3,6-Derivatives of diketopiperazine are prepared in this manner without acetylation of the imino nitrogen. However, as such, the reaction is not general; aliphatic aldehydes do not form simple 3,6-derivatives and, though it is generally applicable to the aromatic series, o-hydroxy-substituted aldehydes give poor yields. By this reaction condensations of vanillin, cinnamaldehyde, piperonal, salicylaldehyde, tolualdehyde and o-chlorobenzaldehyde with glycine anhydride were effected. Diketopiperazine failed to condense with benzylidene aniline on fusion. Likewise, all attempts to condense diketopiperazine with substituted amidines have been unsuccessful.

Diketopiperazine exists, theoretically, in five enol forms



Enol forms Half-enol forms

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[3] Bamberger and Berle, *Ann.*, **273**, 269 ff. (1880); F. Henrich, *Ber.*, **32**, 673 (1899).

[4] Greenwald, This Journal, **47**, 1443 (1925).

[5] Nicolet and Campbell, *ibid.*, **50**, 1115 (1928).

[6] Sasaki, *Ber.*, **54**, 163–171 (1921).

The proof of the presence of the hydroxyl groups in enol-diketopiperazine is based mainly upon color tests such as a positive xanthoproteic and a negative picric acid reaction. Definite confirmation of their presence is furnished by the fact that two molecules of a-naphthyl isocyanate condense easily with one of the diketopiperazine.

It is probable that not more than one or two of the various enol forms exists in more than a negligible amount in the equilibrium mixture. Evidence of the structure of the ordinary form of enol-diketopiperazine may be obtained from the chemical conduct of the a-naphthyl isocyanate derivative.

Since two molecules of the isocyanate react with one of diketopiperazine it seems that the more stable form must contain two hydroxyl groups. It is necessary, then, to decide among forms (1), (2) and (3). When the isocyanate derivative is formed it is evident that an equilibrium mixture of the keto and enol forms is no longer present but that a derivative of one or more of these forms will be produced. Since the reactions of these forms with aldehydes will differ because of their structure, an attempt was made to determine the predominant enol form by condensation with *m*-nitrobenzaldehyde.

If the ordinary enol form is (1), the compound should not condense with aldehydes, for no methylene groups are present; (2) should condense with two aldehyde groups while (3) should react with only one.

On condensation the product showed a nitrogen content of 14.73%. The unexpected fact is that this compound is, according to the analysis, virtually identical with that obtained from the condensation of glycine anhydride and m-nitrobenzaldehyde. Such a derivative has a nitrogen content of 14.73%. If the enol form had been (2), the condensed product would have contained 11.70% nitrogen, and if it had been (3), 13.21%.

The most probable explanation seems to be that during the course of the reaction the isocyanate derivative first hydrolyzed, forming enol-diketopiperazine, which reverted to the more stable keto form and then condensed with the aldehyde. It is to be expected that (2) would condense with the aldehyde without hydrolysis; on the other hand, before (1) could react with an aldehyde, it would necessarily have to hydrolyze. The analysis showed that nearly complete hydrolysis had taken place. This indicates that (1) is the ordinary form of diketopiperazine.

To confirm this statement another condensation was made with tolualdehyde. The condensation product formed from tolualdehyde and glycine anhydride has a nitrogen content of 8.81%. If the conclusion drawn from the preceding analysis is correct, the product resulting from the reaction of the a-naphthyl isocyanate derivative of diketopiperazine with tolualdehyde should agree quite closely with this figure. The compound formed contained 8.92% of nitrogen. The decomposition point of this product also checked closely with that of 3,6-*bis*-tolual-2,5-diketopiperazine. Hence the probability of the carbon–carbon double bond is supported by this reaction.

Other reports on methylene condensations which have been in progress in this Laboratory will appear at an early date.

Experimental Part

1. Creatinine

5-Benzalcreatinine.—The method employed in the preparation of this compound is typical of the derivatives of creatinine which were made. Five grams of creatinine and an excess of benzaldehyde were thoroughly mixed and then heated at 150° in a flask attached to an air reflux. The creatinine dissolved in about forty-five minutes, giving a reddish-yellow solution which formed a yellow solid on cooling. Flaky, golden-yellow crystals were obtained by recrystallization from boiling alcohol. The compound was difficultly soluble in boiling alcohol and water, and slightly soluble in ether, benzene and chloroform; m. p. 244°, uncorrected.

Anal. Calcd. for $C_{11}H_{11}ON_3$: N, 20.89. Found: N, 20.76, 20.64.

Fusion of benzylidene aniline and creatinine (equivalent quantities) for an hour at 150° produced the same compound. Aniline was liberated, as was shown by the bleaching powder test.

5-*m*-Nitrobenzalcreatinine.—Five g. of creatinine and an equivalent quantity of m-nitrobenzaldehyde were fused for three hours at 150°, and then for two hours more at 180". The product was purified by extracting first with alcohol and then with water. It is very slightly soluble in each. A 70% yield of the yellow powder was obtained; it decomposes at 288°, uncorrected.

Anal. Calcd. for $C_{11}H_{10}O_3N_4$: N, 22.76; C, 53.75; H, 4.1. Found: N, 22.63; C, 53.85; H, 4.19.

5-(*m*-Methoxy-*p*-hydroxybenzal)-creatinine.—Half an hour's fusion of equivalent quantities of vanillin and creatinine gave a 75% yield of the condensation product. It was purified by extracting first with alcohol and then with water. It was very slightly soluble in each of these solvents and slightly soluble in ether, chloroform and benzene; it melts with decomposition at 267°, uncorrected.

Anal. Calcd. for $C_{12}H_{13}O_3N_3$: N, 17.0; C, 58.3; H, 5.30. Found: N, 16.78; C, 58.04; 58.06; H, 5.43, 5.55.

II. Diketopiperazine

Preparation of Glycyl-glycine Anhydride.—Diketopiperazine was prepared according to the method of Emil Fischer[7] from glycine ethyl ester hydrochloride.

3,6-Bis-(*m*-methoxy-*p*-acetoxybenzal)-2,5-diketopiperazine.—The method employed in the preparation of this derivative is typical of the 3,6-derivatives which were prepared. One and four-tenths grams of glycine anhydride, 4.5 g. of vanillin, 4 g. of sodium acetate and 8 g. of acetic anhydride were thoroughly mixed and heated at 120–130° for eight hours. During this period the liquid solidified into a brown mass of crystals. After cooling the product was washed several times with hot water and then extracted for a short time with alcohol. The bright yellow crystals were recrystallized from boiling acetic acid and, for analysis, dried for three hours at 130°.

A list of the six aldehyde derivatives is given in Table I. They were prepared in a similar manner. All of this series of compounds are soluble

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[7] Fischer, *Ber.,* 39, 2930 (1906).

in boiling acetic acid, but they are insoluble in water, alcohol, ether, benzene and chloroform.

TABLE I

DATA ON ALDEHYDE DERIVATIVES

3,6-Bis-( )-2,5-diketopiperazine	Formula	Diketopiperazine condensed with	Nitrogen, % Calcd.	Found		Brown at °C.	Dec., °C.
m-Methoxy-p-acetoxy	$C_{24}H_{22}O_8N_2$	Vanillin	6.00	5.88	5.85	290	310
Cinnamal	$C_{22}H_{18}O_2N_2$	Cinnamaldehyde	8.18	8.00		335	350
Piperonylidene	$C_{20}H_{14}O_6N_2$	Piperonal	7.41	7.29		290	320
m-Acetoxybenzal	$C_{22}H_{18}O_6N_2$	Salicylaldehyde	6.90	6.77	6.90	M. p.	255
Tolual	$C_{20}H_{18}O_2N_2$	Tolualdehyde	8.81	8.69	8.80	305	320
o-Chlorobenzal	$C_{18}H_{12}O_2N_2Cl_2$	*o*-Chlorobenzaldehyde	7.80	7.82		330	340

α-Naphthyl Isocyanate Derivative of Diketopiperazine.—One gram of thoroughly dried glycine anhydride was finely powdered and covered with 8 g. (excess) of α-naphthyl isocyanate. The mixture was heated in the sulfuric acid bath to 175'. At this temperature it rapidly turned into a white solid. After fifteen minutes it was cooled. The compound was insoluble in ligroin, ether, water, benzene and chloroform; it was very slightly soluble in boiling acetic acid. To remove the excess isocyanate the mass was extracted with ligroin for three hours; two hours' extraction with water removed any unchanged glycine anhydride. The fine white crystals were dried for three hours at 130°. They melt with decomposition at 232°.

Anal. Calcd. for $C_{26}H_{20}O_4N_4$: N, 12.39. Found: N, 12.15, 12.18.

Condensation of the Isocyanate Derivative with *m*-Nitrobenzaldehyde.—Three grams of the isocyanate derivative, 10 g. of m-nitrobenzaldehyde, 8 g. of sodium acetate and 20 g. of acetic anhydride were heated at 125°. After eight hours the product was cooled, digested with warm water and boiling alcohol, recrystallized from boiling acetic acid and dried for three hours at 130'.

Anal. Calcd. for $C_{18}H_{12}O_6N_4$: N, 14.73. Found: N, 14.38.

Condensation of the Isocyanate Derivative with *m*-Tolualdehyde.—Five grams of the isocyanate derivative, 2 g. of tolualdehyde, 2 g. of sodium acetate and 4 g. of acetic anhydride formed the condensation product on heating for several hours at 125°. It was digested with water and alcohol and recrystallized from boiling acetic acid; yellow crystals, decomposing at 320°.

Anal. Calcd. for $C_{20}H_{18}O_2N_2$: N, 8.81. Found: N, 8.92.

Summary

1. A method of preparation of condensation products of creatinine with aldehydes and benzylidene aniline has been described.

2. Six new derivatives of diketopiperazine with aldehydes have been prepared.

3. The presence of hydroxyl groups in the enol form of diketopiperazine has been confirmed by the formation of the a-naphthyl isocyanate derivative.

4. The a-naphthyl isocyanate derivative condenses with aldehydes only after hydrolysis. It, therefore, appears that the ordinary enol form of diketopiperazine has double bonds between carbon atoms.

COLUMBIA, MISSOURI

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

PARA-CYMENE STUDIES. XII. 2-PARA-CYMYL-4-SEMICARBAZIDE AND CERTAIN DERIVATIVES

BY ALVIN S. WHEELER AND J. G. PARK[1]

RECEIVED MAY 27, 1929 PUBLISHED OCTOBER 5, 1929

This paper presents a continuation of studies of semicarbazides as ketone reagents[2] In view of the fact that cymene is a fair priced product, its derivatives are more available than formerly. Ketone reagents such as hydroxylamine, phenylhydrazine and semicarbazide differ in their properties from strongly basic to neutral. This series is extended in the acid direction by using phenylsemicarbazide with its negative phenyl group and finally the substituted phenylsemicarbazides containing bromine or the nitro group. It is desirable to have such a variety for detecting and characterizing ketones since no one is applicable to all cases.

2-p-Cymyl-4-semicarbazide, not known hitherto, was prepared by known methods. 2-Amino-p-cymene was converted into p-cymylurea, a compound first mentioned by Kremers and Demonbreun,[3] who made only a very brief note about it and gave no analysis. We believe their product was impure since our product melts six degrees higher. Three methods of preparation were tested. The first was Davis and Blanchard's method[4] of preparing phenylurea. An aqueous solution of aminocymene hydrochloride and urea was heated. This was unsatisfactory on account of the simultaneous production of di-p-cymylurea, a compound not hitherto described. The second method was that of Kelbe and Warth,[5] who prepared *m*-cymylurea. The hydrochloride of aminocymene was heated with potassium cyanate. No dicymylurea was produced but the yield was poor. The method adopted was to heat an acetic acid solution of aminocymene with potassium cyanate. In a similar way Walther and Wlodkowski[6] made o-tolylurea. The yield was better and the product readily purified.

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[1] This paper is an abstract of a thesis submitted by J. G. Park in partial fulfilment of the requirements for the degree of Master of Arts at the University of North Carolina in June, 1929.

[2] Wheeler and Bost, THIS JOURNAL, 46, 2813 (1924); Wheeler and Walker, *ibid.*, 47, 2792 (1925).

[3] Kremers and Demonbreun, J. Am. *Pharm. Assocn.*, 12, 591 (1923).

[4] Davis and Blanchard, THIS JOURNAL, 45, 1816 (1923).

[5] Kelbe and Warth, Ann., 221, 171 (1883).

[6] Walther and Wlodkowski, *J. prakt. Chem.*, 59, 266 (1899).

The urea was converted into the cymylsemicarbazide on heating with hydrazine hydrate as Curtius and Burkhardt[7] made phenylsemicarbazide.

Cymylsemicarbazide readily condenses with ketones, forming semicarbazones which are very stable. It was noted that the purely aliphatic and mixed aliphatic-aromatic ketones condensed with great readiness, whereas the purely aromatic ketones as well as camphor and carvone required the presence of some acetic acid and one or more hours of heating.

Experimental

Di-*p*-cymylurea, $(C_{10}H_{13}NH)_2CO$.—(a) A solution of 6 g. of urea and 18.5 g. of aminocymene hydrochloride in 75 cc. of water was boiled until bumping due to separated crystals became violent. The crystals were filtered off and proved to be dicymylurea. They were quite bulky and the weight was extremely small. The filtrate was cooled and the crystals which separated consisted of a mixture of dicymylurea and probably cymylurea. The solution was boiled again until bumping occurred and the process completed as above. The products proved to be the same so the method was given up.

(b) Baeyer's method[8] of preparing phenylurea was found to be much better. Two moles of aminocymene were heated wifh one mole of urea at 150–170° until the evolution of ammonia greatly slackened. This required about three hours. On cooling the mixture solidified. The product was extracted with ligroin and hot dilute hydrochloric acid to remove any unchanged aminocymene and urea. Coloring matter was removed with charcoal. The product crystallized from alcohol in bulky microscopic needles, melting at 240° to a dark brown viscous liquid. It is soluble in chloroform and slightly soluble in ether, benzene and carbon tetrachloride; 1.2 g. of urea gave 1.4 g. of the pure diurea.

Anal. Calcd. for $C_{21}H_{28}ON_2$: N, 8.64. Found: N, 8.79.

***p*-Cymylurea,** $C_6H_3(CH_3)(C_3H_7)NHCONH_2$.—To 74.5 g. of aminocymene dissolved in 200 cc. of warm glacial acetic acid was slowly added with stirring 48 g. of powdered potassium cyanate. After heating nearly to boiling the mixture was poured into a liter of cold water; yield, 84.7 g. The product was recrystallized by dissolving in glacial acetic acid and reprecipitating with water. It was finally recrystallized from 40% alcohol; yield of pure product, 55 g. Cymylurea is soluble in chloroform, moderately soluble in ether and slightly soluble in carbon tetrachloride. It dissolves in warm benzene but on cooling separates as a gelatinous mass. *p*-Cymylurea may also be prepared by the action of potassium cyanate on aminocymene hydrochloride, but the yield is lower.

Anal. Calcd. for $C_{11}H_{16}ON_2$: N, 14.58. Found: N, 14.47.

2-*p*-Cymyl-4-semicarbazide, $C_6H_3(CH_3)(C_3H_7)NHCONHNH_2$.—38.5 g. of cymylurea and 60 g. (2.5 equivalents) of 42% hydrazine hydrate were dissolved in 200 cc. of 95% alcohol and the mixture boiled for thirty hours under a reflux condenser, though not continuously. The solution was filtered hot to remove some black particles and concentrated to one-half of its original volume. A small amount of a yellow oil separated. In order to bring about crystallization some water was added, the mixture was cooled with ice water and vigorously stirred. A mass of yellowish crystals formed weighing 33.5 g. and melting at 96–105°. A saturated ice-cold ether solution was made and treated with a stream of hydrogen chloride. The salt was filtered off, redissolved in warm water and sufficient potassium hydroxide added to precipitate the free base; yield, 25.7 g.

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[7] Curtius and Burkhardt, *J. prakt. Chem., 58,* 205 (1898).

[8] Baeyer, *Ann. Chem. Pharm., 131,* 251 (1864).

The carbazide crystallizes from warm dilute alcohol in colorless microscopic prisms, melting at 112°. It is soluble in benzene, ether, chloroform and warm carbon tetrachloride.

Anal. Calcd. for $C_{11}H_{17}ON_3$: N, 20.28. Found: N, 19.77.

The hydrochloride forms colorless microscopic needles from water, melting at 166–168° with decomposition. The melting point varies somewhat with the rate of heating.

Anal. Calcd. for $C_{11}H_{17}ON_3 \cdot HCl$: HCl, 14.97. Found: HCl, 14.86.

Semicarbazones.—The semicarbazones were prepared by dissolving one mole of cymylsemicarbazide in alcohol (1 g. per 10 cc. of alcohol) and adding two moles of the ketone. Unless otherwise stated crystallization of the carbazone began at once. The mixture was heated for ten minutes on the steam-bath and cooled for complete crystallization. The product was recrystallized from alcohol or benzene as found best. All thermometer readings were made with a set of Wheeler Standard Thermometers, each instrument having a small 50-degree scale for complete immersion.

TABLE I

SEMICARBAZONES

	Ketone	Crystal form	Solvent	M p., °C., (corr.)	Liquid
1	Acetone	Fluffy needles	Alcohol	182	Colorless
2	Methylethyl	Rect. plates	Alcohol	182–183	Colorless
3	*a*,γ-Dichloro-acetone	Prisms	Benzene	173	Decomposes
4	Mesityl oxide	Fluffy needles	Alcohol	163	Colorless
5	Acetoacetic ester	Fluffy needles	50% alc.	133.5	Colorless
6	Cyclohexanone	Fluffy needles	Alc.–Bz	192.5	Yellow
7	Camphor	Micro needles	Alc.–Bz	217	Yellow
8	Carvone	Micro prisms	70% alc.	97	Yellow
9	Benzophenone	Fluffy needles	Alcohol	150	Colorless
10	Acetophenone	Fluffy needles	Benzene	212	Colorless
11	Benzoin	Fluffy needles	Alcohol	172	Yellow

1. Soluble in chloroform, benzene, slightly soluble in ether; yield, 90% of weight of semicarbazide. 3. Alcohol for reaction medium not satisfactory. Benzene used. 5. Soluble in chloroform, ether and benzene. 6. Slightly soluble in hot alcohol and in ether. 7. One cc. of glacial acetic acid added to the reaction mixture before heating; mixture heated for two hours. 8. One cc. of acetic acid required and one hour of heating. In order to isolate the product water was added dropwise as long as it dissolved. On cooling a viscous oily product separated. This crystallized on a porous plate after two days. 9. One cc. of glacial acetic acid was added and heating for two and one-half hours was necessary. The crude product was gummy but became crystalline on a porous plate. In recrystallizing from alcohol seeding was a great aid. 10. The product weighed 20% more than the weight of the semicarbazide used. 11. Acetic acid needed and an hour and a half of heating.

TALBE II

ANALYSES OF SEMICARBAZONES

	Formula	Subs., g.	Vol. of N in cc.	Nitrogen, % Calcd.	Found
1	$C_{14}H_{21}ON_3$	0.1437	22.9 (31°, 745.6 mm.)	17.00	16.76
2	$C_{15}H_{23}ON_3$	.1546	23.1 (31°, 748 mm.)	16.09	15.77

TABLE II (Concluded)

	Formula	Subs., g.	Vol. of N in cc.	Nitrogen, % Calcd.	Found
3	$C_{14}H_{19}ON_3Cl_2$	0.1728	22 (31°, 743.3 mm.)	13.29	13.35
4	$C_{17}H_{25}ON_3$	.1396	19.1 (32°, 749.8 mm.)	14.63	14.39
5	$C_{17}H_{25}O_3N_3$	.1737	21.6 (33.5°, 749.5 mm.)	13.16	12.95
6	$C_{17}H_{25}ON_3$	.1535	20.5 (30°, 750.1 mm.)	14.63	14.22
7	$C_{21}H_{31}ON_3$	.1785	21.1 (32.5°, 745.6 mm.)	12.31	12.32
8	$C_{21}H_{29}ON_3$	.1504	18.1 (36°, 748 mm.)	12.39	12.31
9	$C_{24}H_{25}ON_3$	.2103	21.9 (31°, 747.1 mm.)	11.32	10.98
10	$C_{19}H_{23}ON_3$	.1643	21.4 (31°, 746 mm.)	13.59	13.71
11	$C_{25}H_{27}O_2N_3$	.1915	19.0 (34°, 747.3 mm.)	10.47	10.27

Summary

1. Di-*p*-cymylurea is obtained in small amount by the action of urea upon aminocymene hydrochloride in aqueous solution. The best method is to heat aminocymene and urea together at 150–170°.

2. *p*-Cymylurea is best prepared by the action of potassium cyanate upon aminocymene in glacial acetic acid solution.

3. 2-p-Cymyl-4-semicarbazide is best made by the action of hydrazine hydrate on p-cymylurea.

4. p-Cymylsemicarbazide yields semicarbazones with the following ketones: acetone, methyl ethyl ketone, a,y-dichloro-acetone, mesityl oxide, acetoacetic ester, cyclohexanone, camphor, carvone, benzophenone, acetophenone and benzoin. The products are very stable. The reactions are immediate except those with camphor, carvone and the purely aromatic ketones. These require some acetic acid and a period of heating.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

THE INDUCED CHLORINATION OF ETHYLENE DICHLORIDE. THE EFFECT OF OXYGEN UPON THE REACTION BETWEEN ETHYLENE AND CHLORINE

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Gaseous chlorine and gaseous ethylene react to form ethylene dichloride. The reaction takes place upon the surface of the containing vessel.[1,2]

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2 \qquad (1)$$

The reaction rate may be expressed by the equation

$$-\frac{d(C_2H_4)}{dt} = K_a' (C_2H_4)(Cl_2)$$

in which the bracketed formulas represent partial pressures of the respective gases. The specific reaction rate varies with the nature of the

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[1] Stewart and Fowler, THIS JOURNAL, 45, 1014 (1923).

[2] Norrish, J. Chem. Soc., 123, 3006 (1923).

catalytic surface,[3] but under given conditions is constant over wide variations in the pressures of the reactants. The experiments upon which these conclusions are based were carried out in the presence of air and in glass vessels whose surfaces were only superficially dried. Water is known to be a catalyst for the addition reaction.[2,4]

Stewart and Fowler[1] made their experiments at such concentrations that ethylene dichloride did not separate as a liquid. Norrish[2] worked at higher pressures, but states that the specific reaction rate, under the conditions mentioned above, was unaltered by the separation of the liquid. In the total absence of water or other catalyst the reaction does not take place,[3,4] and there is some evidence[1] that the reaction is autocatalytic.

The present paper concerns experiments carried out with thoroughly pure dry reactants and in glass vessels which were evacuated at a pressure of 1 X 10^{-6} mm. of mercury and at a temperature of 500° to remove all traces of water and oxygen from the walls.

Under these conditions there is an inhibition period and the reaction, when once started, is autocatalytic, with a marked increase in reaction rate accompanying the deposition of liquid. Besides the addition reaction, substitution occurs, and the facts suggest that the latter reaction is induced by the former. The effect of oxygen is to decrease the induced reaction, presumably by dissipating the energy of the exothermic addition reaction.

Experimental Method

Description of Apparatus and Preparation of Materials.—Figure 1 shows diagrammatically the reaction system. The apparatus was constructed of pyrex glass. The reaction vessel A was of three hundred cubic centimeters' capacity. All the connecting lines were of 2 mm. inside diameter except that leading from Stopcock 4 into A, which was 1 mm. inside diameter.

A and E and the attached capillaries (to within a few centimeters of the stopcocks) could be baked out at any temperature up to 550° by means of an electric oven. While baking was in progress, the stopcocks were kept cool by a blast of air. After the baking was completed the oven was replaced by an oil thermostat. This was controlled by hand to one tenth of a degree, the oil being pumped around the bulb at a constant rate.

The ethylene was made by dropping ethylene dibromide on zinc. It was washed with 95% alcohol, then passed over calcium chloride and phosphorus pentoxide and liquefied in a liquid air trap. A middle fraction of the liquid ethylene was distilled slowly at low pressure into the ethylene supply system, which was composed of several small traps containing small amounts of phosphorus pentoxide so that the ethylene was continually in contact with the drying agent. Between experiments the ethylene was kept frozen in one of the traps by means of a liquid-air bath. Before each experiment the ethylene system was evacuated for half an hour to an hour to the vapor pressure of solid ethylene.

The chlorine used was taken from a tank of liquid chlorine, passed over calcium chloride and liquefied in a trap with liquid air. The first fourth of the chlorine was

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[3] Norrish and Jones, *J. Chem. Soc.*, **126**, 55 (1926).

[4] Brooks and Humphrey, *J. Ind. Eng. Chem.*, **9**, 750 (1917).

distilled away; the next half of the original was distilled slowly into the supply system at low pressure and sealed off for use in the experiments; it was then handled in a manner similar to that described for the ethylene. Analysis showed that the chlorine contained one and eight-tenths mole per cent. of hydrogen chloride as an impurity. As it subsequently appeared that hydrogen chloride had no important effect on the reactions studied, it was not thought worth while to attempt the removal of the hydrogen chloride.

Other substances were introduced to the reaction bulb through Stopcocks 9, 8 and 5. In the case of vapors they were first liquefied in G and subjected to high vacuum before introduction to A. The course of the reaction was followed at constant volume by means of a double manometer system. One leg of a constant level mercury manometer was connected by a 2-mm. capillary tube to the reaction bulb through Stopcocks 1 and 4. During a reaction the two sides of the mercury column of this manometer were maintained at constant level by adjusting the pressure on a second mercury manometer. The probable error in readings in the rapid reactions was not greater than 1 mm., and the readings for the slow reactions were accurate to 0.5 mm. The ratio of volumes of reaction flask and manometer system was approximately 100:3.

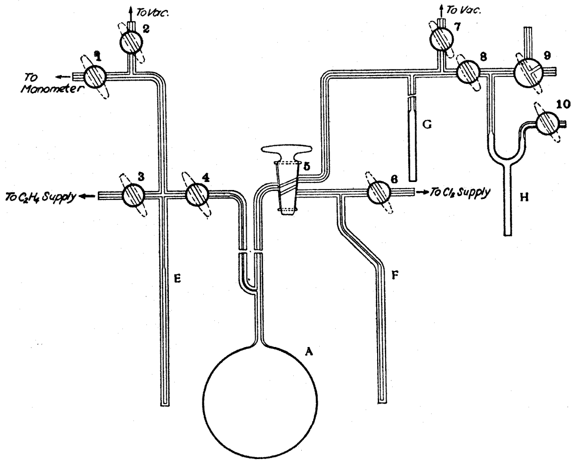

Fig. 1.

Experimental Procedure.—After baking at high temperature under vacuum for several hours, the furnace was removed and replaced by the oil-bath. All light was excluded from A and connections by black coverings. The substance (oxygen, ethylene dichloride, etc.), whose effect was being studied was then introduced through Stopcocks 9, 8 and 5; 5 was then closed and 1 and 4 were opened to determine the pressure of the substance in A. Stopcock 4 was then closed and the manometer system swept out with ethylene, through 3 and 1. Ethylene pressure in E was next built up greater than the pressure in A and 4 opened, the pressure being then increased until the total pressure in the system was equal to the pressure of the substance in A plus the desired pressure of ethylene in A; 4 was then closed and the pressure in the manometer system built up further with ethylene to a few centimeters greater than the expected initial total pressure in A after the introduction of chlorine; 3 was then closed. The desired amount of chlorine from the supply system was liquefied in F at approximately $-30°$. All lights in the room were turned out except the small ruby bulbs on the manometers; 5 was turned to connect F and A and a water-bath placed on F. As soon as the chlorine was evaporated into A, 5 was closed and 4 opened, and the initial total pressure in A noted. Less than a minute elapsed from the time of starting to admit chlorine to **A** to the time of making the first reading. In general an accurate determination of the total initial pressure was obtained; in those cases where the initial reaction rate was rapid, a satisfactory extrapolation to zero time could be made. At the start of the reaction the partial pressure of each substance in the reaction bulb was accurately known. The manometer system contained pure ethylene equal to the total pressure in A and as the reaction progressed some of this expanded into A in amount proportional to the pressure drop. Since the relative volumes of the manometer system and A were known, a correction could be applied for this effect in making rate calculations. Moreover, since this expansion was from the manometer system into the reaction bulb, it served to prevent any substance from leaving the reaction vessel.

The Determination of End-Products.—At the end of the reaction the condensable gases and vapors were frozen out in G or H with liquid air. Any non-condensable gases present were removed through 10. When the pressure in A dropped to zero, 5 was closed and the vapor evacuated through 8 and 9 and through a bubbler containing water. In those experiments where there was an excess of chlorine, potassium iodide was included in the bubbler contents. The iodine was titrated with 0.1 *N* sodium thiosulfate solution and any hydrogen chloride present was determined by titrating with standard sodium hydroxide solution. Ethylene dichloride did not hydrolyze in the time allowed and the amount of hydrogen chloride present did not interfere with the thiosulfate titration. The amounts of the residual gases were expressed in terms of their respective partial pressures.

In most cases there was excess of ethylene at the end of the reaction. The amount of hydrogen chloride formed was a measure of the amount of substitution reaction and. since the initial chlorine was accurately known, it was possible to calculate the amount of addition reaction and hence the amount of ethylene used up. Knowing the amounts of addition product (ethylene dichloride) and substitution product (trichloro-ethane), the volume of the reaction vessel, and assuming Raoult's Law, it was possible to calculate the vapor pressure of the liquid.

The sum of the final hydrogen chloride pressure, the final vapor pressure and the final ethylene or chlorine must be equal to the final pressure observed for the experiment. This was found to be true within a millimeter of mercury pressure in every case.

Experimental Results

When ethylene and chlorine were allowed to react in a darkened glass flask from whose surface all volatile substances had been removed by means of prolonged evacuation at 500°, the following observations were made. There was a short inhibition period. followed by an autocatalytic reaction. The reaction rate became relatively high as soon as the reaction products separated as liquids upon the walls. A high proportion of the reacting chlorine was used up to produce hydrogen chloride, according to the reactions

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2 \qquad (I)$$

$$C_2H_4Cl_2 + Cl_2 \longrightarrow C_2H_3Cl_3 + HCl \qquad (II)$$

Reaction II was not independent of Reaction I. Oxygen gas decreased the total reaction rate and tended to eliminate Reaction II.

The Inhibition Period.—In Fig. 2 the pressure of the reacting system is plotted against the time for several typical experiments carried out in the same vessel. Experiment 4–1 was performed before the reaction flask was evacuated at high temperatures and therefore the form of the plot corresponds closely to those of similar plots previously reported.[1] Succeeding experiments gave erratic results, but in each of them there was marked autocatalysis and indication of a true inhibition period. About twenty experiments were carried out before it was felt that the surface conditions were reproducible, the chief difficulty being complete evacuation of the walls.[5]

In no case, in the absence of oxygen, could the reaction be inhibited for more than a few minutes. The plot of Expt. 5–8 (Fig. 2) shows the effect of 3.1 cm. of mercury pressure of oxygen, in which an inhibition period of fifty-five minutes was observed. It is believed that this inability to prolong the inhibition period indefinitely was due to the autocatalytic feature of the reaction. It started in some unbaked portion of the capillary connections and gradually extended to the reaction flask.[6]

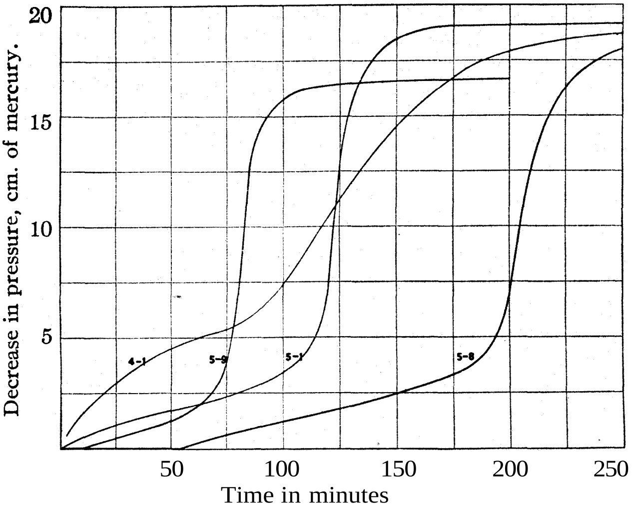

Fig 2.—The effect of surface evacuation and of oxygen upon the catalysis of the reaction between ethylene and chlorine gases. Conditions: Curve 4–1, evacuated at room temperature; Curves 5–1, 5–9, prolonged evacuation at 500°; Curve 5–8, dry oxygen gas introduced after evacuation.

[5] After each experiment the system was evacuated at 100° for an hour; then the temperature was raised to 500° and dry oxygen admitted to burn off any film of carbonaceous matter. The evacuation was then carried to 1×10^{-6} mm. of mercury pressure for several hours before the succeeding experiment. In the earlier experiments there was evidence of incomplete evacuation, since in spite of a very good vacuum before admitting the reactants, some gas which was non-condensable in liquid air appeared after the reaction was over. Eventually this no longer happened.

[6] Nitrogen gas as well as oxygen served to prolong the inhibition period by slowing diffusion in the capillaries. Faulty manipulation of the manometer, causing convection currents in the capillaries, hastened the apparent start of the reaction.

It is important to note that the evacuated surface was not a catalyst for the reaction.

The Substitution Reaction.—As the evacuation of the walls progressed an increasing amount of hydrogen chloride appeared among the reaction products. Under given initial concentrations of reactants, however, this appeared to reach a maximum when about thirty-five to forty mole per cent. of the initial chlorine was used up in the substitution reaction. An attempt was made to increase this amount in two ways, first by introducing ethylene dichloride vapor or liquid as an initial constituent, second, by using a large excess of chlorine over ethylene. The results are presented in Table I, in which the experiment number gives the order in which the experiments were performed although, for the sake of clarity, they are grouped in a different order. The influences of some other factors are also indicated.

Table I

The Effect of Certain Variables won the Chlorination of Ethylene Dichloride During its Formation from Ethylene and Chlorine

Temperature: Expt. 4–1, 26.5"; Expts. 5–1 to 5–9, 18.5°; Expts. 5–10 to 6–11, 20.0°. Initial HCI content, 1.8 mole per cent. of the chlorine

Expt. no.	Initial pressures (cm. of mercury) C_2H_4	Cl_2	Other substances	Molal ratio HCl formed to Cl_2 used up
4–1	17.7	14.7	None (?)	0.08
5–1	16.2	15.1	None (?)	.20
5–3	16.5	15.1	None (?)	.08
5–6	15.8	16.4	None (?)	.19
5–7	16.3	16.4	None	.32
5–9	16.2	16.1	None	.38
6–4	15.9	30.5	$C_2H_4Cl_2$, 3.7	.47
6–5	16.8	7.85	$C_2H_4Cl_2$, 5.4	.47
6–6	16.3	3.0	$C_2H_4Cl_2$, 6.1	.34
6–7	15.9	3.0	$C_2H_3Cl_3$, 1.4	.19
6–10	14 8	5.2	$C_2H_3Cl_3$, 1.6	.26
6–11	5 4	15.0	$C_2H_3Cl_3$, 1.6	.38
6–8	16 3	2.63	$C_2H_4Cl_2 + C_2H_3Cl_3$, 3.8	.33
6–9	5.0	15.1	$C_2H_4Cl_2 + C_2H_4Cl_3$, 3.7	.496
5–4	15 9	15.6	02, 0.1	.17
5–5	15.8	16.3	02, 0.2	.24
5–8	15.3	15.5	O_2, 3.1	.10
6–1	16.6	17.5	O_2, 35.1	.105
6–2	16 8	17.1	O_2, 3.1, $C_2H_3Cl_3$, 1.6	.18
6–3	16.2	17.5	H_2O, 0.1	.31
5–10	16.2	17.1	N_2, 3.0	.39
5–11	16.1	17.2	N_2, 4.7; $C_2H_4Cl_2$, 1.8	.46
5–12	16.5	16.9	N_2, 7.9; $C_2H_4Cl_2$, 6.1	.48
5–2	8.4	7.85	None (?)	.02

A maximum of one-half the reacting chlorine was used in Reaction II, even when excess chlorine remained in contact with the reaction products for a period several times as long as the half period of the reaction itself. This maximum was approached closely only when the vapor phase was initially nearly saturated with ethylene dichloride (6.1 cm. of mercury pressure). Hence in the absence of such vapor, that is, in the initial stages of an experiment such as Expt. 5–7, the reaction was probably largely addition. On the other hand, some substitution took place before the actual separation of liquid. This was shown by a comparison of such plots as appear in Pig. 2, with respect to the magnitude of the observed pressure change at which the reaction became very rapid. When the hydrogen chloride content was high (Expts. 5–7, 5–9) this point corresponded to about three centimeters of mercury, but when it was low (Expts. 4–1, 5–3, 6–1) the pressure change was about five centimeters before the rapid reaction set in. Since the vapor pressures of the ethylene dichloride and trichloro-ethane are, respectively, 6.1 cm. and 1.6 cm. at 20.0°, and since the appearance of a rapid reaction corresponds in time with the separation of liquid, then the compound of low vapor pressure started to form before the gas phase became saturated with ethylene dichloride.

Similarly, Expts. 6–6 and 6–8 suggest that the mere presence of the liquid phase does not ensure the maximum substitution reaction if the ethylene concentration is high and the chlorine concentration low. Experiment ***5–2*** indicates that if both are low in concentration the substitution reaction is inhibited. However, Expt. 6–4, toward its end, duplicated the concentration condition of Expt. 5–2, but with liquid present, and yielded nearly the maximum substitution. There is no doubt that liquid ethylene chloride facilitates the substitution (Reactions I and 11), and that low concentrations of reactants favor addition only.

The presence of trichloro-ethane apparently decreased the chance of the substitution reaction (Expts. 6–11 and 6–9).

Oxygen gas definitely tends to decrease the amount of Reaction II but does not entirely eliminate it on an evacuated surface. It also causes Reaction I to go more slowly, although this effect will be made the subject of a separate paper. A small amount of oxygen is almost as effective as a large amount. Attempts were made to reproduce the original glass surface by exposing it to moist air at 100° for several hours, cooling the system and then evacuating at room temperature. In every instance the freshly adsorbed gas was quickly removed, giving rise to the characteristic substitution reaction. On the other hand, the original surface was difficult to evacuate.

Nitrogen gas and water vapor had no apparent effect upon the induced substitution reaction.

Other investigators[4] report the formation of trichloro-ethane as a side reaction during the addition of ethylene to chlorine. That it was the sole product of substitution in this case is made probable by the facts mentioned above. Further, the total reaction products from several experiments were collected in Bulb G (Fig. 1) by condensation in liquid air and then allowed to evaporate. After the ethylene and hydrogen chloride had volatilized, the remaining liquid was condensed in E (Fig. 1) and its vapor pressure measured at 20.0°. The liquid was then allowed to distil slowly into A and the vapor pressure of the residue measured from time to time. The vapor pressure slowly dropped from 5.8 cm. of mercury to 1.5 cm., at which point about 7% of the original liquid remained, and finally to 1.2 cm. when 2% of the liquid remained. Since the higher chlorinated ethanes have still lower vapor pressures, it is apparent that they were not present in appreciable quantities.[7]

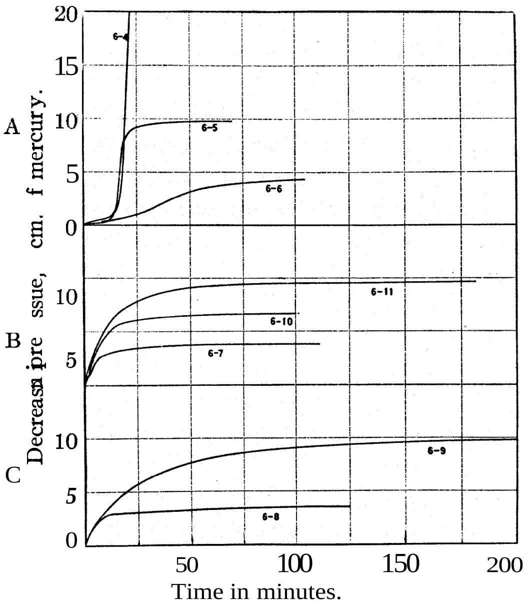

Fig. 3.—Catalysis of the reaction between ethylene and chlorine gases by (A) ethylene dichloride vapor, (B) trichloro-ethane vapor, (C) the mixed liquids.

The Catalyst.—The existence of an inhibition period in the presence of an evacuated surface, with or without oxygen gas, and in the presence of hydrogen chloride, indicated that none of these or any combination of them was a catalyst. Experiments were therefore made with the other products of the reaction, ethylene dichloride and trichloro-ethane, present at the start of the reaction. The results are presented graphically in Fig. 3. In Expts. 6–4, 6–5 and 6–6 ethylene dichloride vapor was used as a possible catalyst (see Table I). In Expts. 6–7, 6–10 and 6–11 pure trichloro-ethane vapor was present at the beginning of the reaction; in Expts. 6–8 and 6–9 the mixed liquids were present.

In each case using the ethylene dichloride vapor, the initial reaction

[7] It was found impossible to separate fully the liquid reaction products by such distillations because of the small amount available. The above measurements indicated the futility of an analysis of the mixture. The total liquid formed and collected could be measured in volume from the known dimensions of the bomb G. It always corresponded within experimental error (5%) to the volume of liquid to be expected from the reactants and hence the carbonaceous film left upon the glass constituted but a minute fraction of the total products.

rate was very low, suggesting in fact a short inhibition period.[8] The autocatalytic part of these reactions could be due either to an approach to saturation of the vapor, with eventual separation of liquid, or to the production of trichloro-ethane, or both. The absence of any suggestion of an inhibition period in those experiments in which trichloro-ethane vapor was initially present indicates definitely that this compound was a catalyst. The above-mentioned curves represent the experimental observations and take no account of the larger pressure changes to be expected, for a given amount of ethylene reacted, after the saturation of the gas phase with vapor. In every case liquid started to separate some time before the maximum reaction rate was reached. This showed that a relatively large amount of liquid was necessary to produce the optimum catalytic conditions, perhaps because it first separated in droplets rather than as a coherent surface film.

In the absence of oxygen, either liquid, or a mixture of them, is a powerful catalyst, but in the presence of oxygen, or upon an unbaked surface, the separation of liquid is not accompanied by a large increase in specific reaction rate (Expts. 4–1 and 5–8, Fig. 2 and Ref. 2).

It may be concluded that upon an evacuated surface the trichloro-ethane vapor is a more powerful catalyst than is the ethylene dichloride vapor; that upon an evacuated surface in the presence of oxygen the addition reaction is catalyzed by the vapors, but less effectively than in its absence; and that upon an unevacuated surface neither vapor is an effective catalyst. The liquids are each effective catalysts but apparently less effective in the presence of oxygen. The order of their catalytic activity in the absence of oxygen is undetermined, but in the presence of oxygen ethylene dichloride is somewhat the better catalyst.[9]

Discussion of Results

The Induced Substitution Reaction.—Since ethylene dichloride is not ordinarily chlorinated under the conditions of time and temperature of the experiments described above, the formation of the trichloro-ethane is brought about as a result of the addition reaction. The course of the reaction and the role of the oxygen may be represented as follows. The starred formulas represent either molecules of sufficiently high energy content to react, as compared to the unstarred molecules of average energy content, or complex compounds with the catalyst. The equilibria indicated by the arrows are arbitrary assumptions.

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[8] The initial abnormal pressure drop in Expts. 6–6 and 6–7 was possibly due to experimental difficulty. It occurred also in Expt. 5–1 (Fig. 2). If it be significant, it would suggest a rapid reaction involving a small amount of adsorbed ethylene.

[9] The experimental data upon which this conclusion is based are not included in this paper; the difference in the catalytic activity is small (40%), hence it may be presumed that any mixture of the two liquids insures constant catalytic activity.

$$\begin{array}{llll} C_2H_4^* + Cl_2^* & \longrightarrow & C_2H_4Cl_2^* \xrightarrow{Cl_2} C_2H_3Cl_3 + HCl + \text{Heat} \\ \ \ \updownarrows \qquad \ \ \downuparrows & & \\ C_2H_4 \qquad Cl_2 & & C_2H_4Cl_2^* \xrightarrow[\text{Wall}]{O_2} C_2H_4Cl_2 + \text{Heat} \\ & & \\ & & C_2H_4Cl_2^* \xrightarrow{C_2H_3Cl_3} C_2H_4Cl_2 + \text{Heat} \end{array}$$

In the absence of the addition reaction ethylene dichloride molecules do not become activated sufficiently for chlorination.[10]

The fact that the presence of liquid ethylene dichloride, at least in the form of a film, increases the chance of the substitution, suggests the transfer of the activation energy to other molecules of the same kind. In effect the liquid dilutes the various deactivators and prolongs the life of the activated form, but this view requires the assumption of relatively slow dissipation of the activation energy among ethylene dichloride molecules as compared to a thermal equilibrium rapidly established in the presence of oxygen or of trichloro-ethane.[11,12]

In view of the facts regarding the catalysis of the reaction it appears likely that the molecular species represented by the symbols $C_2H_4^*$ and Cl_2^* are in reality complex aggregates of ethylene and chlorine with ethylene dichloride or trichloro-ethane. These aggregates may be within the liquid film or adsorbed upon the glass surface. That the latter concept is important is suggested by the fact that a trace of adsorbed gas within the walls during the early experiments reduced the amount of the substitution reaction, and was itself displaced and appeared in the gas phase at the conclusion of the reaction. These effects could have occurred only if the reaction involved the glass surface. On the other hand, if this were the only reaction area, the separation of liquid should introduce a diffusion factor and decrease the rate of the reaction. Since the presence of a liquid film increased the reaction rate it must be assumed either that there is a rapid homogeneous reaction within the film, or that the liquid surface is a better catalyst or that some other influence increases the reaction rate. These factors will be considered in detail in a separate communication. It is sufficient to note now that when the glass surface with adsorbed water is itself a catalyst (Expt. 4-1, Fig. 2) not only is the amount of substitution reaction diminished but also the catalytic effect of the condensing vapor is lessened. When the surface is not a catalyst, due to evacuation of water from it, oxygen gas reduces both the amount of substitution and the reaction rate, even in the presence of

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[10] The chlorine used in the substitution may or not require independent activation. Another alternative assumption would utilize the energy of reaction to activate the chlorine to a degree sufficient for the substitution of an unactivated ethylene dichloride molecule.

[11] Christiansen and Kramers, Z. *physik. Chem.*, 104, 451 (1923).

[12] N. A. Milas, *Proc. Nat. Acad. Sci.*, 14, 844 (1928), presents a case of induced polymerization of styrene and refers to other results of a similar character.

the liquid. It seems probable (1) that the glass surface functions as an adsorbing medium for any catalyst; (2) that the reaction is normally initiated on this surface; *(3)* that the energy liberated by the reaction may be transmitted to a liquid film if the glass is slow to adsorb it; (4) that this energy may induce the substitution reaction; *(5)* that in the absence of light and water[13] the normal liquid phase reaction is very slow; (6) that in the absence of deactivators a liquid-phase addition reaction may be induced by the glass surface reaction; (7) that oxygen is neither a catalyst nor an inhibitor for the addition reaction, but serves very effectively in maintaining equilibrium in the thermal distribution among the molecules, thus preventing induced or chain reactions.[14]

The Specific Reaction Rate.—By assuming that after the separation of the reaction products as liquids the catalytic conditions were constant, the rates of the reaction under different conditions may be compared. The law governing the rate may be expressed

$$-\frac{d(C_2H_4)}{dt} = K'' (C_2H_4)(Cl_2) \qquad (1)$$

In order to evaluate the concentrations of the reactants at any instant from their initial concentrations and from the measured change in pressure, the amount of the substitution reaction taking place and the vapor pressure of the deposited liquid must be known.

Consider first the case that the reaction is simple addition. If a and b are the initial pressures of ethylene and chlorine, respectively, and x the amount, expressed in pressure, of ethylene that has reacted, then

$$\frac{dx}{dt} = K_a'' (a - x)(b - x) \qquad (2)$$

Since the rate-determining step of the substitution reaction is this same reaction, but for each ethylene molecule reacting two chlorine molecules are used up, then for a reaction in which the maximum of substitution occurs the expression becomes

$$\frac{dx}{dt} = K_s'' (a - x)(b - 2x) \qquad (3)$$

The numerical values of K_a'' and K_s'' should be identical under given catalytic conditions. In this paper it is intended to establish only that the above expressions are true within certain limits, namely, in the presence of oxygen to insure Reaction I (addition) as the main reaction and in the presence of excess chlorine (but no oxygen) to insure the maximum of substitution (Reactions I and II). Under these conditions the specific

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[13] H. S. Davis, THIS JOURNAL, 50, 2769 (1928).

[14] The fact that the reaction takes place only upon the surface (or liquid film) would minimize the importance of radiation as a means of transfer of energy from one molecule to another. Moreover, the reaction as studied in this paper was very susceptible to light from electric globes, which brought about a gas-phase reaction. This effect is under investigation.

reaction rates are the lowest obtained for an evacuated surface. Under other conditions the reaction was faster and the specific reaction rates were not constant during the period of constant catalytic conditions.[15]

Tables II and III present the data as calculated from the experimental observations (see section on Experimental Procedure). In Expt. 6–1 (Table II) the values of K_a'' are not calculated from the beginning because of the separation of liquid during the reaction, with attendant change in the catalytic surface. Also it was impossible to interpret the observed change in pressure in the presence of partial substitution; hence it was assumed that all of this substitution occurred in the early stages of the reaction while the chlorine concentration was high. Similarly in Expt. 6–9 (Table III) the small amount of simple addition was presumed to occur after the chlorine concentration became low.

The agreement of the two specific reaction rates with each other is very good in consideration of the assumption regarding equal catalytic activity

TABLE II

EXPERIMENT 6–1

The specific rate of formation of ethylene dichloride from gaseous ethylene and chlorine, in the presence of 35.1 cm. of oxygen gas and with the liquid reaction products condensed on an evacuated glass surface. Chlorine was used up in substitution (10.5% of initial chlorine) during the first part of the reaction only. Pressures are in centimeters of mercury and time is in minutes.

$$K_a'' = \frac{2.3}{(a - b)t} \log \frac{b(a - x)}{a(b - x)}$$

Time, min.	Vapor pressure, cm.	C_2H_4 pressure, a, cm.	Cl_2 pressure, b, cm.	$K_a'' \times 10^3$
0	0.00	16.6	17.40	
460	4.60	8.66	7.16	
470	4.85	7.28	5.73	3.2
480	5.00	6.23	4.63	3.6
490	5.08	5.51	3.86	3.6
500	5.15	5.01	3.31	3.4
510	5.18	4 62	2.87	3.5
520	5.20	4 32	2.54	3.1
530	5.21	4.08	2.28	2.9
540	5.22	3 90	2.08	2.6
550	5.23	3.77	1.94	2.0
575	5.25	3.48	1 65	1.8
600	5.27	3.25	1.41	1.9
625	5.28	3.06	1.21	2.0
650	5.29	2.89	1.03	2.3
703	5.30	2.62	0.75	2.3
792	5.30	2.40	.52	1.7
852	5.30	2.25	.37	2.5
912	5.30	2.14	.25	3.1
1000	5.30	1.90	.00	Av. 2.6

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[15] The reason for this is suggested in Factor 6 in the preceding section. It will be discussed in detail in a later paper.

TABLE III

EXPERIMENT 6–9

The specific rate of formation of 1,2,2-trichloro-ethane from gaseous ethylene and chlorine in the presence of a mixture of ethylene dichloride and trichloro-ethane condensed on an evacuated glass surface. Chlorine was used in simple addition (0.4%) at the end of the reaction only. Pressures are in centimeters of mercury and time is in minutes.

$$K_s'' = \frac{2.3}{2(a - b/2)t} \log \frac{b/2(a - x)}{a(b/2 - x)}$$

Time, min.	Vapor pressure, cm.	C_2H_4 pressure, *a*, cm.	Cle pressure, *b*, cm.	$K_s'' \times 10^3$
0	3.7	5.00	15.10	...
5	3.55	4.07	13.15	2.7
10	3.45	3.43	11.80	2.5
15	3.40	2.92	10.75	2.7
20	3.35	2.57	10.00	2.2
25	3.34	2.29	9.40	2.2
30	3.33	2.05	8.90	2.3
35	3.32	1.83	8.45	2.5
40	3.31	1.64	8.05	2.6
45	3.30	1.48	7.70	2.4
50	3.30	1.31	7.35	3.2
55	3.30	1.20	7.10	2.2
60	3.30	1.10	6.90	2.4
65	3.30	1.01	6.70	2.4
70	3.30	0.93	6.55	2.6
75	3.30	.87	6.40	1.8
80	3.30	.82	6.30	1.9
85	3.30	.77	6.22	2.2
90	3.30	.73	6.10	1.5
95	3.30	.705	6.03	1.0
100	3.30	.68	5.98	1.2
00	3.30	.25	4.90	Av. 2.2

in the two cases. The trend of the constants is quite characteristic. In experiments made under other conditions the trend involved from five to ten times this minimum rate, but in such cases the specific reaction rate constant decreased toward the end of the reaction and approached the same value.

Attempts were made to show that the reaction rate was independent of the concentration of the one or other reactant, but without success.

Diffusion in either the gas phase or liquid film is not an important factor in determining the rate; calculations show that for the fastest reactions about 10^5 molecules strike the surface for each one that reacts.

Summary

Under certain circumstances gaseous ethylene and gaseous chlorine react quantitatively to form ethylene dichloride. Under other circumstances they form only 1,2,2-trichloro-ethane and hydrogen chloride. The specific reaction rates for the two reactions are the same. The

substitution reaction is induced by the addition reaction, the heat of formation of ethylene dichloride being utilized to promote the formation of trichloro-ethane.

In the absence of water and light the reactions are autocatalytic.

Oxygen inhibits the utilization of the reaction energy to promote substitution. Nitrogen and water have little effect in this respect. Oxygen and excess chlorine reduce the specific reaction rate to the same minimum value. It is suggested that besides the induced substitution reaction there is also an induced addition reaction.

BERKELEY, CALIFORNIA

[COMMUNICATION NO. 389 FROM THE KODAK RESEARCH LABORATORIES]

THE FRACTIONAL PRECIPITATION OF CELLULOSE ACETATE AND SOME PROPERTIES OF THE FRACTIONS

BY J. G. MCNALLY AND A. P. GODBOUT

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Introduction

It is well known that cellulose acetates may be prepared that have widely different physical properties but identical chemical compositions. These differences are commonly ascribed to some difference in state of aggregation or molecular weight of the cellulosic micelles. Several synthetic organophilic colloids—polyvinyl acetate,[1] polyindene,[2] polycinnamalfluorene[3] and polystyrene[2]—have been shown to be mixtures of polymers representing a rather wide range of polymerization of the monomer; it also has been shown that the physical properties of these colloids are intimately connected with the range of sizes of the molecular aggregates present.

The easiest method yet found for fractionating such mixtures is a precipitation process which makes use of the fact that the more highly polymerized components are the first to precipitate from a solution when a precipitating liquid is added. It has been found possible to adapt this method to the case of cellulose acetate and show that a representative material is a mixture of acetates having widely different characteristics.

Materials.—All the experiments reported here were made on a single sample of cellulose acetate prepared by subjecting a dope acetylated triacetate to acid hydrolysis until the product was soluble in acetone. The acetyl number determined by the Eberstadt[4] method was 44.50.

Methods of Fractionation.—Two procedures were used to separate

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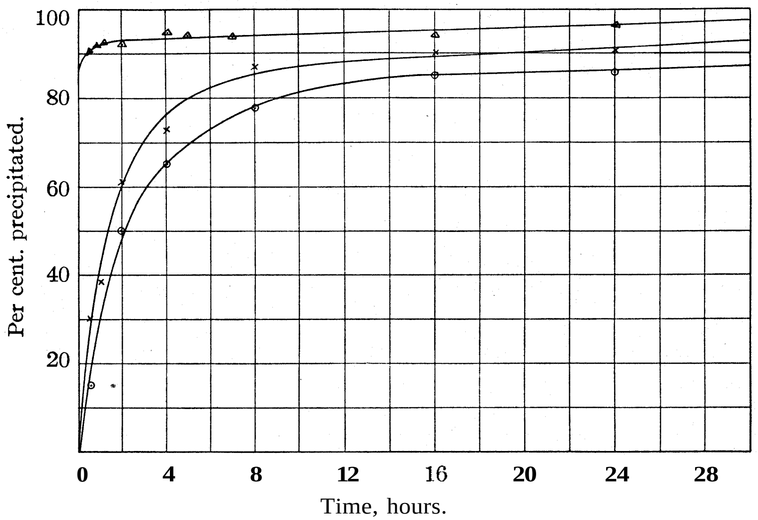
[1] G. S. Whitby, J. G. McNally and W. Gallay, *Trans. Roy. Soc. Canada*, *22*, *27* (1928).

[2] H. Staudinger, *Ber.*, *59*, 3019 (1926).

[3] G. S. Whitby and J. R. Katz, THIS JOURNAL, *50*, 1160 (1928).

[4] Eberstadt, "Dissertation," University of Heidelberg, 1911; Knoevenagel, *Z. angew. Chem.*, *27*, *507* (1914).

the cellulose acetate into fractions. In Method A a 10% solution of the acetate in acetone was made and either water or a mixture of three parts of water and one of acetone added in insufficient amount to completely precipitate the acetate. It is essential that the formation of large clots of precipitate be avoided if a true fractional precipitation is to be effected. In our experiments the precipitation was carried out in a 250-cc. centrifuge bottle fitted with a rubber stopper provided with holes for the shaft of *a* Cenco stirrer and the tip of a buret. The solution to be fractionated was placed in the bottle and water added slowly through the buret, rapid stirring being maintained during the operation. Near the latter end of the precipitation, it is advantageous to substitute a **3**:1 mixture of water and acetone as the coagulating liquid. The precipitated acetate was separated by centrifuging and more precipitant added to the liquid. In this manner a series of fractions was obtained that differed in their solubility in acetone–water mixture.



⊙, **34%** water; ×, 36% water; △, **45%** water.

Fig. 1.

On attempting to repeat quantitatively the fractionation outlined above, it was found that the amount of acetate that could be separated on centrifuging under standard conditions depended very much on how long the solution was allowed to stand after the precipitant had been added.

Fig. 1 shows the percentage of acetate separated by centrifuging partially precipitated solutions that had been allowed to stand for different periods of time after the addition of 34, 36 and 45% of water to a 10% solution of the acetate in acetone. A convenient method of fractionation consists, then, in adding a suitable amount of water to the acetone solution of cellulose acetate and collecting the precipitates that form after various lengths of time. This will be called Method B. By controlling the length of time the solution stands before centrifuging, Method A could he quantitatively repeated. Fig. 2 shows the percentage of cellulose acetate precipitated by various water concentrations after standing for thirty minutes. The water concentration is given as percentage by volume of the total amount of liquid.

Changes in the Properties of Cellulose Acetate Caused by Precipitation, Drying and Re-solution.—De Mosenthal[5] found that the viscosity of cellulose nitrate was *decreased* by repeated precipitation and re-solution while McBain[6] states that cellulose nitrate recovered from solution either by evaporation or precipitation is more insoluble and gives solutions of *higher* viscosity than the original material. No similar experiments appear to be on record for cellulose acetate, but if any difference in the properties of fractions collected by either Method A or B is to be attributed to the heterogeneity of the original material, it should first be shown that the treatment involved in the precipitation process does not appreciably alter the characteristics of the acetate. To obtain data on this point, 500 g. of a 10% acetate solution in acetone were precipitated by thoroughly mixing with 2 liters of distilled water. The precipitate was dried to a constant weight at 105° and a 5-g. sample set aside. The remainder was redissolved and the procedure repeated until all of the acetate was used up. In Table I the acetyl numbers and viscosities of 4% acetone solutions are given. Sample A was precipitated once, B twice, etc. Viscosity measurements were made at 25° with an Ostwald viscometer. The samples did not give sharp melting points but they all showed the same behavior on heating, softening at 255–260° and decomposing at 260–265°.

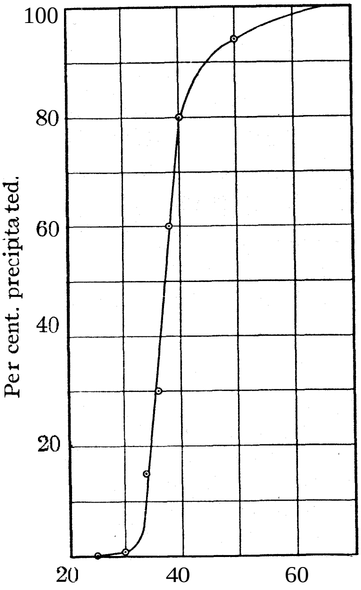


Fig. 2.

These experiments indicate that not much change is produced by repeatedly precipitating cellulose acetate. An increase in viscosity of **13%** showed after nine precipitations. It will be noted from the table that a small part of the acetate was lost during each precipitation. This portion

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[5] H. de Mosenthal, *J. Soc. Chem. Ind.*, *30*, 782 (1911).

[6] J. W. McBain, C. E. Harvey and L. E. Smith, *J. Phys. Chem.*, *30*, **347** (1926)

TABLE I

ACETYL NUMBERS AND VISCOSITIES

Sample	Acetate in soln., g,	Acetate recovered, g.	Recovered, %	Viscosity, centipoises	Acetyl number
Original	..	..	..	6.85	40.4
A	50	49.1	98.2	6.75	40.6
B	45	43.4	96.5	7.05	40.5
C	39	38.1	97.8	7.25	40.45
D	33	32.7	99.2	7.35	40.6
E	27	26.0	96.4	7.51	40.4
F	21	21.0	100	7.56	40.5
G	16	15.4	96.3	7.60	40.45
H	10	9.3	93.0	7.78	40.6
I	5	4.6	92.0	7.72	40.45

remained suspended in the water as a finely divided suspensoid and the increase in viscosity may be reasonably attributed to the loss of this probably less highly polymerized fraction rather than to any change in the remaining fraction. It will be noted that in Fraction F, where this suspended material was collected by filtration, only a very slight increase in viscosity was noted over the preceding sample.

Melting Points, Acetyl Numbers and Viscosities of the Fractions.—Typical results obtained by both methods of fractionation will now be given.

Method A.—Seventy grams of cellulose acetate was dissolved in 630 g. of acetone and 250 cc. of water and 250 cc. of 3:1 water–acetone mixture was added. The precipitate collected was labeled Fraction A. One hundred and twenty-five cc. of the 3:1 mixture was added to the filtrate and Fraction B separated. Fraction C was obtained on the addition of 120 cc. of water to the filtrate from B. On distilling off the acetone from the filtrate from C, Fraction D was obtained.

Fraction A contained the bulk of the precipitate. About 80% of this material was dissolved in 500 cc. of acetone, and 153 cc. of water and 180 cc. of 3:1 mixture were added to give Fraction A-1. This filtrate was mixed with 25 cc. of 3:1 mixture and Fraction A-2 precipitated. The addition of 170 cc. of 3:1 mixture to this filtrate gave A-3, and A-4 appeared on distilling off the acetone from the filtrate from A-3.

Fraction A-1 was then refractionated as follows. The precipitate was dissolved in 300 cc. of acetone and 110 cc. of water added. The resulting precipitate was marked A-1-a. The addition of 25 cc. of water and 100 cc. of 3:1 mixture precipitated A-1-b; 150 cc. of water added to this filtrate gave A-1-c. A-1-d was obtained by distilling the acetone from the filtrate of A-1-c.

The melting points, acetyl numbers and viscosities of these fractions are given in Table II, with their weights and the composition of the liquid from which they precipitated.

Method B.—Thirty-six per cent. of water was added to a 10% solution of cellulose acetate in acetone and the precipitate separated after the mixture had been standing for thirty minutes at room temperature. The filtrate was then set aside and allowed to stand for four hours, when it was again centrifuged and a fraction obtained. Two other fractions were obtained in like manner and the data for all of them are given in Table III.

TABLE II

PROPERTIES OF CELLULOSE ACETATE FRACTIONS OBTAINED BY METHOD A

Fraction	Weight. g.	% Original wt.	Water by vol. when pptd., %	Acetyl number	M. p., °C.	Viscosity, centipoises
Original	..	..	...	40.4	266	6.68
A	15.7	24.1	32	39.6	287	5.28
B	6.2	9.5	35	39.7	250	4.08
C	6.65	10.2	39	39.9	236	1.68
D	2.6	4.0	100	39.9	217	0.65
A-1-a	0.6	0.9	27	39.65	301	..
A-1-b	10.1	15.5	32	39.2	292	23.6
A-1-c	4.0	6.2	44	39.6	264	7.16
A-1-d	0.05	0.08	100	39.6	255	..
A-2	10.3	15.9	33	40.4	264	9.41
A-3	6.2	9.5	39	..	255	3.79
A-4	0.7	1.1	100	39	240	

TABLE III

PROPERTIES OF CELLULOSE ACETATE FRACTIONS PREPARED BY METHOD B

Fraction	Elapsed time, hours	Per cent. pptd.	Viscosity, centipoises	Acetyl number	M. p., °C.
A	0.5	49.5	12.85	40.6	270
B	4.5	7.75	4.96	40.8	257
C	22.5	14.50	4.32	40.8	252
D—Residue, filt. from C.		21.25	2.22	40.8	239

Specific Rotation.[7]—The optical rotary powers of Fractions A, B, C and D were determined by using the green mercury line (546 mμ) in a 20-cm. tube. The solvent was a mixture of 85 parts of chloroform and 15 of alcohol by volume. At a concentration of 1% the observed α for each of the fractions was —0.34" and $[\alpha]_{546}^{20} = -17°$.

The data in the two preceding tables make it clear that the original sample of cellulose acetate was a mixture of a large number of components with widely different physical constants. The acetyl numbers of all of the fractions remained sensibly constant, indicating that an explanation of the difference in properties is not to be found in a difference in the degree of acetylation of the components. This conclusion receives further support in the constancy of the specific rotation. The changes in melting point, viscosity and solubility of fractions of the same chemical constitution all point to the conclusion that the original cellulose acetate contains a series of micelles differing either in the number of elementary glucose anhydride units they contain or in the manner in which they are joined together to form the micelle. In this respect cellulose acetate resembles the synthetic organophilic colloids already mentioned.

Solubility of Cellulose Acetate Fractions in Organic Liquids.—Cellulose acetate fractions that were separated by a procedure that made use of

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[7] We are indebted to Mr. Murray of the Organic Research Laboratory for these measurements of optical rotation.

their different solubilities in acetone–water mixtures might well be expected to show different solubility relationships in other solvents. Such was found to be the case. The fractions used in these solubility tests were prepared by Method B. The concentration of water was 36%. Fraction A was collected after standing for twenty minutes and contained 29.7% of the original acetate; B, three hours, 17.85%; C, twenty hours, 28.5%. D was obtained by adding a large volume of water to the filtrate of C and amounted to 19.3% of the original.

Solubility was estimated by placing about 0.1 g. of the sample in a test-tube and adding 20 cc. of the liquid in question. The test-tube was stoppered and placed on a tumbling machine for twenty-four hours. The appearance of the samples was noted at frequent intervals during this time and final notations were made three days later.

The data obtained in these tests are compiled in Table IV, these observations representing the final condition of the acetate.

TABLE IV

THE SOLUBILITY OF CELLULOSE ACETATE FRACTIONS IN ORGANIC LIQUIDS

Solvent	Fraction[a]				Solvent	Fraction[a]			
	Esters					Alcohols			
	A	B	C	D		A	B	C	D
Methyl formate	4	5	5	5	Methyl alcohol	0	0	0	0
Ethyl formate	4	5	5	5	Ethyl alcohol	0	0	0	0
n-Propyl formate	2	3	4	5	Benzyl alcohol	2	2	2	2
Methyl acetate	4	5	5	5	Cyclohexanol	0	0	1	4
Ethyl acetate	1	1	3	5		Ketones			
n-Propyl acetate	0	0	0	1	Di-methyl ketone	5	5	5	5
n-Butyl acetate	0	0	0	1	Methyl ethyl ketone	4	5	5	5
n-Heptyl acetate	0	0	0	0	Di-ethyl ketone	0	0	1	2
Isopropyl acetate	0	0	0	1	Cyclohexanone	5	5	5	5
Phenyl acetate	5	5	5	5	Methylcyclohexanone	4	5	5	5
Benzyl acetate	4	4	4	5		Halogenated hydrocarbons			
Kesorcinol acetate	4	5	5	5	Chloroform	5	5	5	5
Methyl phthalate	4	5	5	5	Bromoform	0	0	0	0
Ethyl phthalate	0	0	1	2	Trichloro-ethane	5	5	5	5
Butyl phthalate	0	0	0	1	Tetrachloro-ethane	5	5	5	5
Mono-acetin	5	5	5	5	Pentachloro-ethane	3	4	4	5
Tri-acetin	0	1	1	1	Dichloro-ethylene	2	2	2	3
					Trichloro-ethylene	1	2	2	3
					Tetrachloro-ethylene	1	2	2	2

[a] The meanings of the symbols are as follows: 0, insoluble, that is, no apparent change; 1, slightly swollen; 2, highly swollen—almost solated; 3, turbid solution; 4, blue opalescent solution; 5, clear solution.

It appears on examination of the above data that the fractions of cellulose acetate that precipitate first from an acetone–water mixture are more insoluble in solvents in general than are those which precipitate later. It will be remembered that the observations recorded in the table were made after the cellulose acetate had been in contact with the solvent for three days and, therefore, indicate an equilibrium state of affairs with no description of the rate at which this equilibrium was reached. In every case where all the fractions ultimately dissolved, the rate of solution was invariably in the order D:C:B:A. Thus, with methyl acetate, the D fraction dissolved in eight minutes, C in twenty minutes, B in one hour and **A** in three hours.

All the fractions show a greater tendency to swell and dissolve in the lower member of an homologous series. If the most prominent atomic grouping in the cellulose acetate molecule is taken, as $\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}O{-}CO{-}CH_3}$, it may be said in a broad sense that cellulose acetate tends to swell and dissolve in those liquids that resemble it most closely in chemical structure. This is in general agreement with the views of Sheppard[8] and Whitby.[9]

Summary

1. A sample of a commercial acetone-soluble cellulose acetate has been fractionally precipitated. The fractions have the same chemical composition but different physical properties; this has been attributed to a difference in the state of aggregation of the glucose anhydride units in the micelles.
2. The solubility of cellulose acetate in organic liquids has been shown to be a function of its state of aggregation as well as its acetyl content.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

THE REDUCTION POTENTIALS OF VARIOUS PHENANTHRENEQUINONES

BY LOUIS FREDERICK FIESER

RECEIVED MAY 31, 1929 PUBLISHED OCTOBER 5, 1929

The problem of correlating the structures of the quinones with their reduction potentials divides itself naturally into two distinct parts: a comparison of the potentials of the parent quinones which are derived from the various aromatic hydrocarbons and heterocycles, and a study of the manner in which substituent groups influence the oxidizing power of a given substance. The results of the present electrochemical study of a number of quinones of the phenanthrene series thus fall into two groups and each of these may be considered in the light of one or the other of the two aspects of the general problem.

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[8] S. E. Sheppard, *Nature*, 73, March 17 (1921).

[9] G. S. Whitby, "Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York City, Vol. IV, 1926, p. **203.**

1. Isophenanthrenequinones.—While all of the homonuclear quinones of benzene, naphthalene and anthracene have been investigated by the electrochemical method, and while rational interpretations have been found for the values of the reduction potentials of these substances, only one of the four possible homonuclear phenanthrenequinones, the 9,10-derivative, has been studied and no adequate account of the potential of this compound has been given. With the object of completing the data for this series, and with the hope that an explanation of the potential of 9,10-phenanthrenequinone might be suggested by a knowledge of the values for the isomeric quinones, 1,2-, 1,4 and 3,4-phenanthrenequinone and a few of their substitution products have been prepared[1] and the normal reduction potentials have been determined by standard methods.

The results are summarized in Table I. The normal potential, E_0, was determined by the electrometric titration of a solution of either the oxidant or the reductant, as indicated by the nature of the titrating reagent. This potential is equal to the e.m.f. of the cell Pt | Solvent, Oxidant, Reductant || Solvent, H_2 | Pt, at the point of half-reduction or half-oxidation. Under ΔE_1 and ΔE_2 are given the average differences between E_0 and the potential at 20% and at 80% reduction or oxidation. The theoretical value is 17.8 mv. The two unsubstituted ortho-quinones, Nos. 1 and 3, are destroyed by an acidic solution too rapidly to permit the preparation and titration of a solution of the oxidant, but the reductant could be titrated so rapidly that the decomposition of the quinone involved an error which was estimated to be less than 3 mv.

TABLE I

REDUCTION POTENTIALS AT 25°

Solvents: A, 0.1 N HCl; B, 50% Alcohol, 0.1 N in HCl and 0.2 N in LiCl

No.	Compound	Solvent	Titrated with	E_0, v.			ΔE_1, mv.	ΔE_2, mv.	E_0(av.), v.
1	1,2-Phenanthrenequinone[1b]	B	$C_6Br_4O_2$[a]	0.650	0.652	0.651	18.5	18.5	0.651
2	1,2-Phenanthrenequinone-4-sulfonic acid[1b]	A	$TiCl_3$	.651	,651	.651	18 9	19.0	.651
		B	$TiCl_3$	.685	.685		17 1	17 4	.685
3	3,4-Phenanthrenequinone[1a]	B	$C_6Br_4O_2$	.615	.614		19 7	21.2	.615
4	3,4-Phenanthrenequinone-1-sulfonic acid[1a]	A	$TiCl_3$	.664	.664	.663	16.9	18 6	.664
		B	$TiCl_3$	.677	.677		17.2	17.8	.677
5	1-Methyl-5,6-(1,2-naphtho)-3,4-coumaranquinone[1a]	B	$TiCl_3$	.461	.460		18 3	17.9	.461
6	1,4-Phenanthrenequinone[1d]	B	$C_6Br_4O_2$	.522	.524	.524	20 0	19 3	.523
7	2-Hydroxy-1,4-phenanthrenequinone[1b]	B	$TiCl_3$	.410	.411	.409	17.9	17.9	,410
8	2-Methoxy-1,4-phenanthrenequinone[1b]	B	$TiCl_3$	.418	.418	.418	18.0	18 3	.418
9	3-Hydroxy-1,4-phenanthrenequinone[1a]	B	$TiCl_3$	.395	.396	.396	17.7	17 4	.396
10	3-Methoxy-1,4-phenanthrenequinone[1a]	B	$TiCl_3$	.408	.409	.410	18 4	18.1	.409

[a] Tetrabromo-o-benzoquinone.

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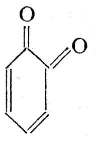
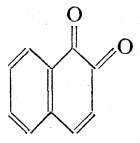
[1] (a) Fieser, THIS JOURNAL, 51, 940 (1929); (b) 51, 1896 (1929); (c) 51, 1935 (1929); (d) 51, 2460 (1929); (e) 51, 2471 (1929).

Examination of the table will show that the relationships between the ortho- and para-isophenanthrenequinones and between the substituted and unsubstituted members of the series are much the same as those found with the corresponding naphtho- and anthraquinones, though there are some deviations for which it is not easy to account. Thus the'two ortho quinones, Nos. 1 and 3, differ considerably in potential, though their sulfonated derivatives, Nos. 2 and 4, are quite similar. From the fact that 3,4-phenanthrenequinone differs in potential from its sulfonate and from 1,4-phenanthrenequinone by normal increments, while the corresponding differences for 1,2-phenanthrenequinone are smaller than would be anticipated, it may be argued that it is 1,2-phenanthrenequinone which exhibits a somewhat abnormal character.

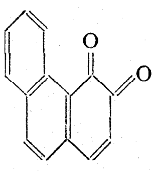
With this minor irregularity, the isophenanthrenequinones form a distinct group, and it is important to establish the exact relationship between this and other series of quinones. A comparison of the normal reduction potentials of the ortho quinones I-V will show that there is little similarity between the two phenanthrene derivatives III and IV or between the isophenanthrenequinone, III, and the isoanthraquinone, V. The difference between 3,4- and 9,10-phenanthrenequinone is not surprising in view of the fact that the former has a terminal quinonoid nucleus while in the latter the quinone grouping is flanked by benzene rings. That 1,2-anthraquinone has a peculiarly low potential has been attributed[4] to a unique structure of anthracene, and the present results furnish no indication that this interpretation should be altered.



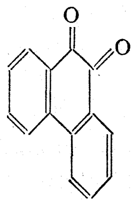
$E_0 = 0.783$[2]
I



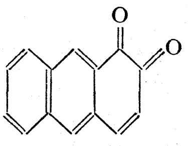
$E_0 = 0.579$[2]
II



$E_0 = 0.615$
III



$E_0 = 0.458$[3]
IV



$E_0 = 0.490$[4]
V

It will be observed that the potential of 3,4-phenanthrenequinone is of the same order of magnitude as that of β-naphthoquinone, and this suggests that the isophenanthrenequinones should be considered in comparison with the corresponding naphthoquinones. Such a comparison,' given in Table II, indicates that the isophenanthrenequinones are higher in potential than the naphthoquinones by a fairly regular increment. The chief structural difference between the two series, or between the quinones II

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[2] Conant and Fieser, THIS JOURNAL, 46, *1858 (1924).*

[3] Fieser and Ames, *ibid.*, 49, 2654 *(1927).*

[4] Fieser, *ibid* , 50, 465 (1928).

TABLE II

DIFFERENCE IN POTENTIAL BETWEEN ISOPHENANTHRENEQUINONES (X) AND NAPHTHOQUINONES (–Y) IN MILLIVOLTS

Substituent	None	$-SO_3H$	$-OH$	$-OCH_3$	$-CH_2CH(CH_3)O-$
1,2-Phenanthrenequinones	+72	4-21, 49[a]			
3,4-Phenanthrenequinones	+36	+34, 41"			+55
1,4-Phenanthrenequinones	+30		+40, 54 ——	56, 65[b]	
Average difference, 48 mv.					

[a] The two figures give the differences observed in solvents **A** and B, respectively.

[b] The first figure refers to the 2-derivative, the second to the 3-substituted isomer.

and III, is that in the tricyclic compounds a naphthylene, rather than a phenylene, group is attached to the quinonoid nucleus. The presence of the phenylene group is responsible for a decrease in the reduction potential of o-benzoquinone amounting to 204 mv. (compare I and 11), an effect which has been attributed to the stabilization of the benzoquinone by the incorporation of one of the otherwise reactive quinonoid ethylene linkages in an aromatic ring.[2] In the same way 3,4-phenanthrenequinone may be regarded as o-benzoquinone with a fused-on naphthylene group, and this group may be said to produce a decrease in the potential of 168 mv. (compare I and III). That the effect is less than for the phenylene group is entirely consistent with the fact that naphthalene is a more reactive hydrocarbon, that it is less ‹'aromatic," than benzene.

That a reasonable interpretation of the potentials of the isophenanthrenequinones is thus found in comparing these compounds with the naphtho- and benzoquinones, is of assistance in seeking an explanation of the potential of 9,10-phenanthrenequinone. The value is abnormally high, that is, it is 83 mv. higher than one would be led to expect from the relationship between quinones I and II. This means either that 9,10-phenanthrenequinone possesses an added reactivity or that its hydroquinone is abnormally inert. Since 1,2-, 1,4- and 3,4-dihydroxyphenanthrene appear to be quite normal, it is highly probable that this is also true of the 9,10-derivative and hence that an account of the observed deviation is to be sought in the structure of 9,10-phenanthrenequinone.

Two explanations of the peculiarly great oxidizing power of 9,10-phenanthrenequinone suggest themselves. The molecule appears to be in a condition of some strain and it is possible that this strain is the result of a configuration in which the two benzene rings are coplanar but not co-axial, the nuclei being spread apart by the carbonyl groups on one side of the diphenyl linkage. It is also possible, and perhaps somewhat more probable, that the two benzene rings are co-axial but not coplanar, that is, that, owing to the normal spatial requirements of the carbonyl groups, the diphenyl skeleton suffers a distortion or twisting which produces a strain within the molecule. It may be possible to distinguish between these two hypotheses, for according to the latter suggestion a monosubstituted phenanthrenequinone should have an asymmetrical configuration.

2. **Substituted 9,10-Phenanthrenequinones.**—Table III summarizes the results of a study of a number of compounds of the type indicated.

TABLE III

REDUCTION POTENTIALS AT 25°

Solvents: A, 0 1 N HCl; B, 50% Alcohol, 0 1 N in HCl and 0.2 N in LiCl; C, 37% Alcohol, 0 047 M in KH_2PO_4 and 0.047 M in Na_2HPO_4; D, 95% Alcohol, 0.2 N in HCl and 0.2 N in LiCl.

No.	-Phenanthrenequinone	Solvent	Titrated with	E_0, v			ΔE_1, mv.	ΔE_2, mv.	E_0 (av), v.
11	Phenanthrenequinone	A							0 442[3]
		B							458[3]
		C	$K_3Fe(CN)_6$	0 460	0 459	0 461	19 3	18 9	460
		D					..	..	471[2]
12	1-Hydroxy-[1d]	B	Quinone	408	408		2 1 2	2 5 7	408
13	2-Hydroxy-[5]		$TiCl_3$	457	.457		18 3	18.3	457
			$TiCl_3$	459	459		18 5	18 6	459
14	3-Hydroxy-[6]	B	Quinone	405	405	404	18 3	19 3	405
15	4-Hydroxy-[7]	B	$TiCl_3$	459	458	458	51	35	458
16	1,2 Dihydroxy-[1c]	B	Quinoue	379	381	.379	18 9	19 5	380
17	1,4-Dihydroxy-[8]	B	Quinone	379	380	379	20 3	22 5	379
18	3,4-Dihydroxy-[1a]	B	Quinone	355	386	384	18 3	18 6	.385
19	2,6-Dihydroxy-[1e]	B	Quinone	401	401	402	20 2	20 4	401
20	2,7-Dihydroxy [1e]	D	$TiCl_3$	448			18 2	17 8	448
21	3,6 Dihydroxy-[1e]	D	$TiCl_3$	344	345	344	19 6	18 9	.344
22	1,2,4-Trihydroxy-[1c]	B	Quinone	340	340	340	18 8	20 4	340
23	1,3,4-Trihydroxy-[1c]	B	Quinone	281	281	281	19 7	22 1	281
24	3-Acetoxy-[6]	B	Quinone	467	467	.467	21 9	19 7	.467
25	3,4-Diacetoxy-[1a]	B	Quinone	488	489	488	20 8	19 2	.488
26	3-Methoxy-[6]	B	$TiCl_3$	421	419	418	18 9	18 8	419
27	3,6-Dimethoxy-[1e]	D	$TiCl_3$	387	387	388	17 7	18 5	387
28	2-Amino-5.9	C	$K_3Fe(CN)_6$	444	443	443	18 7	18 7	.443
		B	$TiCl_3$	493	.490	,490	19 9	20 1	491
29	3-Amino-'0	C	$K_3Fe(CN)_6$	362	361	.362	18 5	18 8	.362
30	4-Amino-9	C	$K_3Fe(CN)_6$	432	432		18 3	18 1	432
31	1-Methyl-11	B	$TiCl_3$	394	394		20 5	25 5	.394
32	1-Methyl-7 *iso*propyl-	D	.					..	4082
33	3-Bromo-[12]	D	$TiCl_3$	500	499	499	18 0	18 5	499
34	2 Nitro [7,13]	D	$TiCl_3$	540	540	540	18 7	18 7	.540
35	3-Nitro-10814	D	$TiCl_3$	562	562	562	18 2	18 3	.562
36	4-Nitro-7.13	D	$TiCl_3$	528	528		17 2	18 0	.528
		B	$TiCl_3$	513	513		18 4	21 1	.513
37	2,5-Dinitro-[15,16]	D	$TiCl_3$	569	570		18 2	18 1	.569
38	2,7-Dinitro-[15]	D	$TiCl_3$	590	590		16 6	17 9	.590
39	( )-1-Sulfonic acid[1a]	A	$TiCl_3$	464	465	465	19 8	20 9	.465
40	( )-2-Sulfonic acid[17]	A	$TiCl_3$	466	466	466	20 3	20 1	.466
		B	$TiCl_3$	490	490		18 4	17 9	490
41	( )-3-Sulfonic acid's	A	$TiCl_3$	472	472	472	20 2	20 0	.472
42	3-Cyano-[18]	D	$TiCl_3$	546	547	548	19 0	19 6	547
43	( )-3-Carboxylic acid[18]	D	$TiCl_3$	520	,519	520	16 5	20.3	520
44	Methyl ( )-3-carboxylate[19]	D	$TiCl_3$	529	529	530	18 6	17 9	529
45	3-Benzoyl-[20]	D	$TiCl_3$	.530	531	530	17 6	18 0	.530
46	5,6 - Dihydroxy - 1,4-naphthoquinone[21]	B	Quinone	427	427	426	19 5	19.9	.427

[5] Schmidt and Spoun, Ber., **55,** 1194 (1922).

[6] Werner, *Ann.*, 322, 135 (1902).

[7] Schmidt and Schairer, ***Ber.,*** 44, 740 (1911)

[8] Brass and Stadler, ***ibid.,*** **57,** 133 (1924). The sample was kindly supplied by Professor Brass, to whom the author wishes to express his thanks.

The quinones which have been described by other investigators were prepared according to the methods indicated in the references and purified until they corresponded in properties to the best samples known. The electrometric titration curve often reveals the presence of an impurity, and in one case, that of 4-hydroxyphenanthrenequinone, the sample appeared to be somewhat contaminated and the results may be somewhat in error for this reason.

An explanation must be given of the considerations which determined the choice of solvent and the method of measurement employed. The most convenient means of determining the reduction potential of a quinone in an acidic solution consists in the electrometric titration of the oxidant with titanous chloride, but this reagent often forms complex compounds

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[9] Brass and Ferber, *ibid.,* 55, 541 (1922).

[10] Brass and Nickel, *Ann.,* **441,** 217 (1925).

[11] Pschorr, *Ber.,* **39,** 3106 (1906).

[12] Schmidt and Lumpp, *ibid.,* **43,** 423 (1910).

[13] Schmidt and Austin, *ibid.,* **36,** 3730 (1903).

[14] Schmidt and Söll, *ibid.,* **41,** 3679 (1906).

[15] Schmidt and Kämpf, *ibid.,* **36,** 3738 (1903).

[16] Schmidt and Kämpf, *ibid.,* **36,** 3745 (1903). Regarding the structure, see, Christie and Kenner, *J. Chem. Soc.,* 470 (1926); Christie, Holderness and Kenner, *ibid.,* 671 (1926).

[17] Sandqvist, *Ann.,* **379,** 79 (1911).

[18] Werner, *ibid.,* **321,** 248 (1902).

[19] Phenanthrene-3-carboxylic acid (ref. 18) was converted by the action of methyl iodide on the silver salt into the methyl ester: colorless plates, m. p. 97°. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.00; H, 5.10. This was oxidized at 70° in the usual manner and the quinone was crystallized from glacial acetic acid, giving orange-yellow needles, m. p. 212°. Calcd. for $C_{16}H_{10}O_4$: C, 72.17; H, 3.79. Found: C, 71.86; H, 3.94.

[20] A solution of phenylmagnesium bromide was slowly added to a stirred and well-cooled solution of 3-phenanthroyl chloride (distilled and crystallized from ligroin, m. p. 118°) in benzene. The benzoyl-3-phenanthrene which resulted was not obtained in a pure condition, for the reaction product was an oil which failed to solidify. Oxidation of this oil with chromic acid in glacial acetic acid solution yielded an orange oil from which 3-benzoylphenanthrenequinone was obtained easily by crystallization from glacial acetic acid. The quinone forms golden-yellow plates melting at 205–206°. The substance is not easily burned. Analyses in a copper oxide tube, even with the use of the Dennstedt contact star, gave low values for carbon. The difficulty was overcome completely by the use of a combustion tube packed with small lumps of fused lead chromate, and by heating the tube to a full red glow. Calcd. for $C_{21}H_{14}O_3$: C, 80.75; H, 3.87. Found: C, 80.59; H, 4.04. This procedure, which was suggested by an observation of Bamberger and Hooker, *Ann.,* **229,** 118 (1885), has been of great service in the analysis of certain other substances which could not be burned completely either by the platinum star method or with the use of cuprous chloride according to Haas, *J. Chem. Soc.,* **89,** 570 (1906).

[21] Dimroth and Roos, *Ann.,* **456,** 177 (1927). The author wishes to thank Professor Dimroth for kindly furnishing him with a sample of this substance.

with substances having ortho hydroxyl groups or with o-hydroxyquinones. For this reason it seemed expedient in many cases to prepare a solution of the reductant by catalytic hydrogenation and to titrate with an organic oxidizing agent such as benzoquinone. It was found that nitrophenanthrenequinones can be reduced to the hydroquinones by titanous chloride in acid solution without reduction of the nitro group; a sharp inflection of the titration curve occurred at a point corresponding to just two equivalents of reducing agent. There were indications that the nitrohydroquinones slowly undergo a disproportionation after the end-point has been reached, but this does not affect the results of the titration.

The solvent most generally employed was a 50% alcoholic hydrochloric acid solution containing lithium chloride to increase the sensitivity of the readings; in some cases a higher concentration of alcohol was required to bring the quinone into solution. It has appeared to the author advisable to compare the potentials of the various quinones under conditions which permit of no dissociation of moderately acidic or basic groups of either the oxidant or the reductant. For this reason, in studying the aminophenanthrenequinones, a solvent ("C") was selected which is probably about neutral and in which the amino group doubtless is undissociated. In one case (No. 28) results in an acidic solution are also included, though they are of little value for the purpose of relating potential and structure.

In the case of the acetoxy-, the di- and triacetoxyphenanthrenequinones, a number of which were studied, it was found that a group in the 1-position interfered with the attainment of electrode equilibrium and the results were not satisfactory. Hydroxyl and sulfonate groups in this position exhibited no such influence, but with 1-methylphenanthrenequinone a constant potential was reached only very slowly.

Considerable information is available from previous work concerning the effect of substituents in a quinonoid nucleus on the potential of a quinone, but little is known regarding substitutions at points more distant from the quinone grouping except that the effect is considerably less. The phenanthrenequinones afford a particularly favorable series in which to study such substitutions because the number of possible isomers is great and because the potential of the parent quinone is subject to considerable change as the result of substitution. Thus the potential range of the quinones here studied is from 0.281 to 0.590 v.

The most striking and novel feature of the results given in Table III is the pronounced influence of the position of a substituent on the potential. A hydroxyl group in the 1-position causes a decided drop in the potential of phenanthrenequinone, the effect is negligible in the 2-substituted isomer, a considerable lowering is produced by substitution in the 3-position and 4-hydroxyphenanthrenequinone has the same potential as the parent compound. This seems rather surprising until it is considered that the 1- and

3-positions are ortho and para, respectively, to one of the quinonoid carbonyl groups, while the 2- and 4- are meta positions. It is not odd that the effect of the hydroxyl group in the ortho and para positions, or in the two meta positions, is about the same. This regularity is not confined to the hydroxyl group or, indeed, to groups which cause a lowering in the potential. Table IV shows that a para amino group lowers the potential considerably more than does a meta-(2) group or a meta-(4) group. A para nitro group produces a greater increase in the potential than does a nitro group in either of the meta positions.

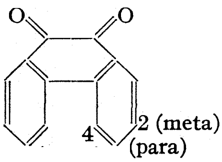


TABLE IV

THE INFLUENCE OF THE POSITION OF THE SUBSTITUENT

Effect in millivolts on the potential of substituting a group in the positions

Substituent	Ortho-Para 1	Ortho-Para 3	Meta 2	Meta 4
OH	**−50**	−53	− 1	0
NH2	. .	−98	−17	−28
NO_2	. .	+91	+69	+57
SO_3H	+21	+30	+24	. .

In the case of the sulfonic acid group the influence on the potential is so slight that the effect of the position of the substituent may well be masked. There is sufficient evidence to warrant the generalization that the effect on the potential of a substituent in the ortho (1) and para (3) positions is about the same, and that it is greater than the effect of a group in either meta position (2 or 4). This conclusion harmonizes well with the known facts concerning the directive influence of substituents in the benzene ring.

The next point of interest is to compare the effects produced by the different kinds of substituent groups. In view of the above generalization, the most favorable series for such a study is that of the 1- or 3-substituted phenanthrenequinones, and one is justified in comparing a 1-derivative with a 3-derivative. This has been done in constructing Table V, though the results for both positions are included wherever available. The figures represent the differences in the potentials of the substituted and unsubstituted quinones in the same solvent. In a few instances two such comparisons are possible for a single substituent.

TABLE V

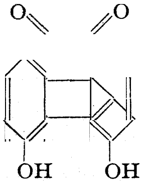
THE EFFECT ON THE POTENTIAL OF PHENANTHRENEQUINONE OF VARIOUS SUBSTITUTENT GROUPS IN THE ORTHO-PARA (1 OR 3) POSITIONS

Substituent	Effect on potential, mv.	Substituent	Effect on potential, mv.	Substituent	Effect on potential, mv.
NO_2	+91	*COOH*	+49	OCH_3	−39
CN	+76	**Br**	+28	*OH*	−50, 53
COC_6H_5	+59	SO_3H	+23, 30	CH_3	−64
$COOCH_3$	+58	$OCOCH_3$	+ 9	NH_2	−98

From the results given in the table it will be seen that all of the unsaturated substituent groups cause an increase in the potential of phenanthrenequinone. The nitro group is the most effective, the sulfonic acid group is the least so and the cyano, ketone and carboxylate groups occupy intermediate positions. Methoxyl, hydroxyl, methyl and amino groups all lower the potential of the parent quinone. The effect of an hydroxyl group is eliminated, and to a slight extent reversed, by acetylation. In general, an ortho-para directing group lowers the potential and a meta directing group causes an increase, though the bromine atom constitutes an exception to this rule, for the substitution of hydrogen by bromine results in an appreciable increase in the potential. Aside from this exception, and aside from the fact that the effect of a methyl group appears to be surprisingly pronounced, the order here indicated for the various substituents is much the same as that found by other methods of comparison. The exact theoretical significance of the present results is not yet completely clear, for there are certain complicating aspects of the whole question of the effect of substituent groups on the potential. Thus, for example, it is not easy to decide whether the substituent alters the nature of the oxidant, of the reductant or of both components of the reversible system. Experiments designed to settle this and other points are now in progress and a more thorough consideration of the above comparison of groups will be reserved until this work is completed.

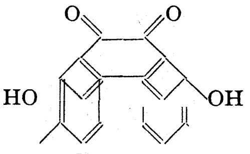
The potentials of the polysubstituted phenanthrenequinones would present a perplexing problem if one had no knowledge of the difference between the ortho-para and the meta types of substitution. Thus 3,6-dihydroxyphenanthrenequinone, VI, and the 2,7-isomer, VII, differ in potential by 104 mv., but this difference is understandable when it is observed that in one case each hydroxyl group is para to a quinonoid carbonyl group while in the other compound both hydroxyls are in meta positions. Furthermore, the difference in potential between 3,6-dihydroxyphenanthrenequinone and 3(or 6)-hydroxyphenanthrenequinone is nearly the same as that between the mono-substituted derivative and phenanthrenequinone. In other words, the effect of the second substituent is approximately equal to that of the first. In order to determine whether this is generally true, a comparison is given in Table VI of the observed total effect of two or

.VI



$E_0 = 0.344$

VII



$E_0 = 0.448$

more substituents with the effect calculated on the assumption that the influence of each group is the same as in a mono-substitution product.

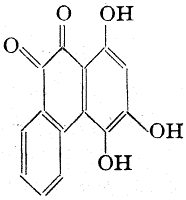
TABLE VI

THE EFFECT OF POLY-SUBSTITUTION

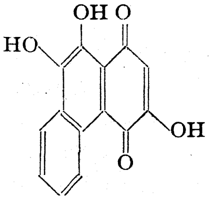
Substituents	Positions of substituents	Effect of substituents on the potential, mv. Found	Calcd.	Diff.
1,2-$(OH)_2$	*o, m*	−78	−51	−17
1,4-$(OH)_2$	*o, m*	−79	−50	−19
3,4-$(OH)_2$	*p, m*	−73	−53	−20
2,6-$(OH)_2$	*m, p*	−57	−53	−4
2,7-$(OH)_2$	*m, m*	−23	−2	−21
3,6-$(OH)_2$	*p, p*	−127	−106	−21
3,6-$(OCH_3)_2$	*p, p*	−84	−74	−10
2,5-$(NO_2)_2$	*m, m*	+98	+126	−27
2,7-$(NO_2)_2$	*m, m*	+119	+138	−19
1,2,4-$(OH)_3$	*o, m, m*	−118	−51	−68
1,3,4-$(OH)_3$	*o, p, m*	−177	−103	−74

It will be observed that with the disubstituted phenanthrenequinones the calculated value is in every case slightly more positive than the value found. The difference is remarkably constant, the average being 18 mv., and this is true regardless of whether the substituents raise or lower the potential and of whether they are situated in the same or in different rings. It appears that the effect of a second substituent is greater by about 18 mv. than that of the first; if the potential is increased (or decreased) by a single substitution, it is increased (or decreased) to a slightly greater extent by a second such substitution, regardless of the positions. From the results with the two tri-substituted quinones it may be concluded that the potential lowering produced by three hydroxyls is greater than that expected from the known effect of each separate group by about 72 mv. The influence of a substituent thus becomes progressively greater as substitution proceeds.

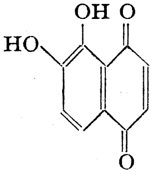
One further question of interest in connection with the present results is that of the possible tautomerism of certain of the hydroxyphenanthrenequinones. It is conceivable, for example, that 1,3,4-trihydroxyphenanthrenequinone, VIII, as the result of a tautomeric change, exists largely in



VIII



IX



X

the form of the para quinone, IX. There is some chemical evidence in support of Structure VIII,[1c] and it is of interest to inquire if this conclusion is in accord with such electrochemical evidence as is available, The reduction potential of the quinone is 0.281 v., a value which appears to be consistent with Structure VIII, though it does not necessarily confirm this structure. One can arrive at a prediction concerning the potential of a quinone having the structure of IX by considering that it is derived from 5,6-dihydroxy-1,4-naphthoquinone, X, by the attachment of a phenylene and an hydroxyl group. Thus: potential of IX = 0.427 v. (5,6-dihydroxy-1,4-naphthoquinone) + [0.396 v. (3-hydroxy-1,4-phenanthrenequinone) − 0.356 v. (3-hydroxy-1,4-naphthoquinone)] − [0.523 v. (1,4-phenanthrenequinone) − 0.396 v. (3-hydroxy-1,4-phenanthrenequinone)] = 0.340 v. This calculation gives a result which is much higher than the potential found for the compound. According to the theory that an hydroxyquinone should exist in that tautomeric form having the lowest possible reduction potential,[22] this means that the quinone in question does not have the structure of IX, a conclusion which is consistent with the other evidence. Similar reasoning supports the 9,10-phenanthrenequinone structure for all of the hydroxy quinones studied.

Summary

The normal reduction potentials at 25° of 43 phenanthrenequinones have been determined and an analysis of the data has led to the following conclusions: (1) an isophenanthrenequinone, such as 1,4-phenanthrenequinone, has a somewhat higher potential than the corresponding naphthoquinone; the difference results from the substituting of a naphthylene group for the less reactive phenylene group. (2) The abnormally high potential of 9,10-phenanthrenequinone is due to a strain resulting from some peculiar spatial arrangement of the molecule. (3) Among the substituted 9,10-phenanthrenequinones, a group has the same effect on the potential when it is ortho or para to a quinonoid carbonyl group and the effect is much greater than when the substituent occupies either of the meta positions. A second substituent has a somewhat greater influence than the first. The potential is increased by the substitution of nitro, cyano, ketone, carboxyl, bromo and sulfonate groups; it is decreased by amino, alkyl, hydroxyl and methoxyl groups.

BRYN MAWR, PENNSYLVANIA

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[22] Fieser, THIS JOURNAL, 50, 439 (1928).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF TRIPHENYL LEAD CHLORIDE AND DIPHENYL LEAD DICHLORIDE

BY HENRY GILMAN AND JACK D. ROBINSON

RECEIVED JUNE 1, 1929 PUBLISHED OCTOBER 5, 1929

Introduction

In connection with studies on organolead compounds a need was felt for a satisfactory method for the preparation of triaryl lead chlorides and diaryl lead dichlorides. We selected the chlorides in preference to the other halides for three reasons: first, the chlorides are more stable than the bromides and iodides; second, they are less expensive than the other halides, assuming that all of them can be prepared in approximately equal yields; and, third, there is no essential difference in reactivity between the several halides in our particular studies.

Triphenyl lead halide, $(C_6H_5)_3PbX$, and diphenyl lead dihalide, $(C_6H_5)_2PbX_2$, have generally been prepared from tetraphenyl lead, $(C_6H_5)_4Pb$, which is obtainable in satisfactory yield from the reaction between lead chloride and phenylmagnesium bromide.[1] Triphenyl lead bromide has been prepared in excellent yields by Grüttner[2] from tetraphenyl lead and the bromine addition compound of pyridine, at low temperatures obtained with solid carbon dioxide. Objections to this method are the expense of pyridine and the inconvenience of using solid carbon dioxide. Krause and Reissaus[3] prepared triphenyl lead iodide by adding a dilute solution of iodine to triphenyl lead. Krause and Pohland[4] prepared triphenyl lead fluoride by double decomposition of potassium fluoride with triphenyl lead bromide, and Krause and Schlottig[5] prepared triphenyl lead chloride by treating phenylmagnesium bromide with a slight excess of lead chloride. They also observed that triphenyl lead chloride could be obtained in 75% yield by heating tetraphenyl lead with four equivalents of ammonium chloride at 170–180° for twelve hours. This method, however, only gives satisfactory yields with small quantities of compound and is valueless with mixed aryl lead chlorides because of their thermal instability. The method most generally used has been that of Grüttner.[2]

The first diphenyl lead dihalide was prepared by Polis,[6] who obtained diphenyl lead di-iodide from a chloroform solution of tetraphenyl lead and iodine. Later[7] he prepared the corresponding bromide and chloride

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[1] Gilman and Robinson, THIS JOURNAL, 49, 2315 (1927).

[2] Grüttner, *Ber.*, 51, 1298 (1918).

[3] Krause and Reissaus, *ibid.*, 55, 888 (1922).

[4] Krause and Pohland, *ibid.*, 55, 1282 (1922).

[5] Krause and Schlottig, *ibid.*, 58, 427 (1925).

[6] Polis, *ibid.*, 20, 716 (1887).

[7] Polis, *ibid.*, 20, 3331 (1887); see, also, Pfeiffer and co-workers, *ibid.*, 37, 1125 (1904); 49, 2445 (1916).

in like manner using bromine and chlorine. Werner and Pfeiffer[8] incidentally obtained some diphenyl lead dichloride in searching for an addition compound of tetraphenyl lead and hydrogen chloride. Goddard, Ashley and Evans[9] obtained the dichloride from a reaction between tetraphenyl lead and a miscellany of inorganic chlorides. The method most generally used has been that of Polis.[6,7]

The methods described at this time involve the following reactions

$$(C_6H_5)_4Pb + HCl \longrightarrow (C_6H_5)_3PbCl + C_6H_6 \qquad (I)$$

$$(C_6H_5)_3PbCl + HCl \longrightarrow (C_6H_5)_2PbCl_2 + C_6H_6 \qquad (II)$$

These reactions are in agreement with Werner and Pfeiffer's[8] observations that hydrogen chloride reacts with tetraphenyl lead in a dry chloroform solution. Polis,[6] on the other hand, reported that concentrated hydrochloric acid does not react with tetraphenyl lead until heated in a tube at 230°, and then lead chloride results.

In our preparation of triphenyl lead chloride, the hydrogen chloride was bubbled into a warm chloroform solution of tetraphenyl lead until crystals of diphenyl lead dichloride formed. The formation of this insoluble dichloride is an excellent end-point, and the yields are distinctly satisfactory (about 75%). The diphenyl lead dichloride was prepared in practically quantitative yields by merely saturating a benzene solution of tetraphenyl lead with hydrogen chloride.

The high yields of the monochloride and of the dichloride make it possible to prepare the corresponding other halides in either of two ways. First, the following metathetical reactions can be used

$$R_3PbX + NaX' \longrightarrow R_3PbX' + NaX \qquad (III)$$

$$R_2PbX_2 + 2NaX' \longrightarrow R_2PbX_2' + 2NaX \qquad (IV)$$

These reactions are readily carried out in dilute alcoholic solutions.[2,4,10] A second indirect method, and the one which is generally recommended, involves the following reactions[11]

$$R_3PbX + NaOH \longrightarrow R_3PbOH + NaX \qquad (V)$$

$$R_3PbOH + HX' \longrightarrow R_3PbX' + H_2O \qquad (VI)$$

The unusual smoothness of the reactions described at this time has recommended them not only for synthetic purposes (for the preparation of aryl lead halides in general) but also for studies in progress on the relative electronegativities of organic radicals.

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[8] Werner and Pfeiffer, Z. *anorg. Chem.*, **17,** 82 (1898).

[9] Goddard, Ashley and Evans, *J. Chem. Soc.*, **121**, 256, 978 (1922).

[10] Calingaert, *Chem. Reviews,* 2, **43** (1925).

[11] It is probable that the bromides can be prepared in equally good yields after the methods described here for the preparation of the chlorides, that is, from tetraphenyl lead and hydrogen bromide. The hydrogen chloride method also gives excellent yields of the tin mono- and dichlorides. Also, alkyl lead mono- and dichlorides can be prepared in the same high yields as the corresponding aryl halides.

Experimental Part

The following directions are typical of a series of experiments carried out by us.

Triphenyl Lead Chloride.—20.2 g. (0.04 mole) of tetraphenyl lead is dissolved in 300 cc. of boiling chloroform and hydrogen chloride is then bubbled through the solution, which is kept near its boiling point (or it may be refluxed gently) by the application of heat. After about fifteen minutes (depending on the rate of flow of gas) a precipitate of shiny plates of diphenyl lead dichloride starts to form and the stream of gas is quickly shut off. This precipitate resembles greatly a precipitate of mercurous chloride, and is not to be confused with a flocculent precipitate that may form if the tetraphenyl lead is impure or if the gas is introduced very rapidly. The flocculent precipitate need not be removed if it forms, inasmuch as the precipitate of diphenyl lead dichloride is very readily recognized even in the presence of the flocks. After the entry of hydrogen chloride has been terminated, the solution is boiled to complete the reaction with any dissolved hydrogen chloride and the solution is then filtered. The quantity of diphenyl lead dichloride obtained by this filtration is 1.5–2.0%.

The chloroform is removed from the clear solution by distillation from a water-bath. The residue when extracted with two 200-cc. portions of hot alcohol leaves the unaltered tetraphenyl lead (about 20%). The alcohol extract yields the pure triphenyl lead chloride (about 75% yield). Approximately the same ratio of products was obtained from a run starting with 56.7 g. (0.11 mole) of tetraphenyl lead.

Diphenyl Lead Dichloride.—An excess of hydrogen chloride is run into a solution of 51.5 g. (0.1 mole) of tetraphenyl lead in 500 cc. of benzene warmed to about 50°. The flask may be open or closed, but one advantage of a closed system is that it gives an indication of the stage of the reaction from the rate at which the gas is being absorbed. The end of the reaction is not readily determined inasmuch as the hydrogen chloride is very slowly absorbed even when the reaction appears to be completed. A better way is to filter the shiny plates of diphenyl lead dichloride when the reaction appears to be at an end and then pass more hydrogen chloride into the hot filtrate.[12] If there is no additional precipitate the reaction is done. Only a very small quantity of lead chloride forms even after prolonged treatment with hydrogen chloride.[12] The yield is 42.2 g. or 98.5%.

Summary

Triphenyl lead chloride and diphenyl lead dichloride may be prepared in high yields by the action of hydrogen chloride on tetraphenyl lead.

AMES, IOWA

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[12] The mixture should be filtered hot in order to avoid precipitation of any unaltered tetraphenyl lead. Tetraphenyl lead and triphenyl lead chloride are readily soluble in hot benzene.

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXIII. SYNTHESIS AND PROPERTIES OF HYDROXY ALKYLIDENE GLYCOLS AND GLYCEROLS

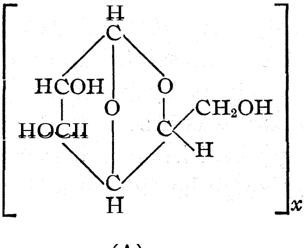
BY HAROLD HIBBERT AND MYRON S. WHELEN[1]

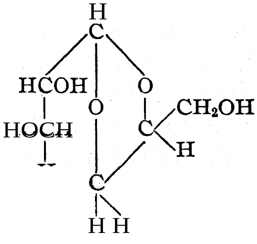
RECEIVED JUNE 7, 1929 PUBLISHED OCTOBER 5, 1929

Investigations dealing with a study of cyclic acetal formation during recent years have dealt almost exclusively with cyclic acetals prepared from saturated derivatives. The tendency of unsaturated aldehydes toward cyclic acetal formation has been but little investigated. The study of this type of cyclic acetal apparently has been rendered difficult by the fact that unsaturated aldehydes, in general, condense only with difficulty with polyhydric alcohols under the experimental conditions usually employed. The use of acid catalysts is disadvantageous, due in many cases to polymerization of the aldehyde. The difficulty appears to lie in the securing of the optimum hydrogen-ion concentration, and failure to undergo condensation may be due to this, coupled with low reaction velocity between the aldehyde and polyhydroxy derivative.

The possibility that the lignin complex, as it occurs in wood, may contain an unsaturated aldehyde grouping,[2] which may be combined with a carbohydrate complex in the form of a cyclic acetal or half acetal, pointed to the necessity for obtaining further information regarding the interaction of unsaturated aldehydes with polyhydric compounds.

Also of added interest is the close connection, as indicated in a previous communication,[3] between cellulose considered as an anhydroglucose (A) and 1,2-dihydroxypropylidene-glycerol-1,2 (2-dihydroxy-ethyl-1,3-dioxolane-4-carbinol) (B), *e.* g.


(A)


(B)

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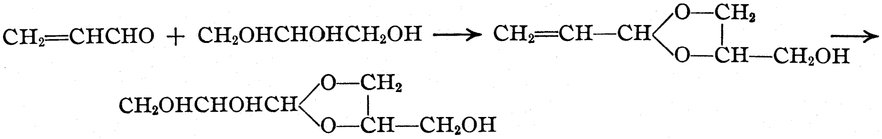
[1] Holder of studentship, Canadian National Research Council. The authors wish to express their thanks to the Canadian National Research Council and the Canadian Pulp and Paper Association for the generous support accorded to them.

[2] Fuchs, "Die Chemie des Lignins," J. Springer, Berlin, 1926, pp. 277–285.

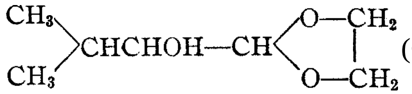
[3] Hibbert and Whelen, THIS JOURNAL, 51, 620 (1929).

For these reasons it seemed of interest to prepare the cyclic acetals involving condensation of acrolein with glycol and glycerol, namely, acrylidene glycol and glycerol, and to use these as initial materials from which, by oxidation, the corresponding dihydroxy derivatives could be obtained



(B)

in order to ascertain how far such structures exhibit a tendency toward polymerization or association.

Investigations on unsaturated cyclic acetal formation have been very limited. Lochert,[4] in an attempt to prepare α-hydroxy-*iso*-amylidene glycol,  (C), by the saponification of α-bromo-*iso*-amylidene glycol, secured a very small amount of what he believed to be the desired compound, (C), but as was to be expected the bulk of the reaction product was the unsaturated cyclic acetal, β-methylcrotonylidene glycol, [2 - (β - methylpropene - 2) - 1,3 - dioxolane], . No investigation of the chemical properties of the unsaturated acetal was made and the presence of α-hydroxy-*iso*-amylidene glycol was not definitely established.

Peacock[6] was the first to prepare cinnamylidene glycerol, and its preparation, properties, etc., have been studied more fully by the present authors.[3]

More recently several unsaturated aldehydes have been condensed with glycol by Hibbert and co-workers[6] to give unsaturated cyclic acetals.

As far as can be ascertained the literature contains no reference to the condensation of acrolein with glycol, and the authors' experiments to bring about such a condensation were unsuccessful. It was, however, possible to prepare the desired acrylidene glycol by indirect synthesis.

The condensation of acrolein and glycerol was first carried out by Nef,[7] who in a study of the dehydration of glycerol isolated a material which he considered to be acrylidene glycerol, though he did not make a detailed investigation of it nor did he establish its identity.

In the present investigation it is shown that the product obtained on heating acrolein with glycerol, without a catalyst, under low pressure, is

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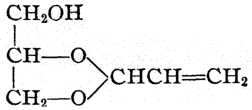
[4] Lochert, *Ann. chim. phys.*, [6] *16*, 26 (1889).

[5] Peacock, J. *Chem. Soc.*, *107*, 816 (1915).

[6] Hibbert, Houghton and Taylor, THIS JOURNAL, 51, 611 (1929).

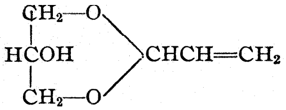
[7] Nef, Ann., 335, 224 (1904).

an acrylidene glycerol which is identical with the material isolated by Nef. This author pointed out that his material could be either of two products (D or E)



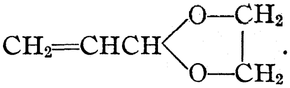
(D)

or



(E)

The present investigation shows that the condensation apparently gives rise to only the five-membered acetal (D). From the point of view of Michael's partition principle the second isomer is probably formed but either in quantity too small to be isolated, or, if in larger amount, it possibly undergoes spontaneous polymerization and remains in the thick, viscous, undistillable residue which is always left in large quantity.

It will be readily observed that with acrylidene glycol only one ring system is possible, namely,  $CH_2{=}CHCH\langle\begin{matrix}O{-}CH_2\\ |\\ O{-}CH_2\end{matrix}$. This product was obtained by indirect synthesis as shown in the experimental part.

These products, acrylidene glycol and glycerol (after determination of the structure of the latter), were then used as convenient starting materials for the preparation of the corresponding dihydroxy derivatives, this being accomplished by oxidation with potassium permanganate at a low temperature.

Of the two dihydroxy acetals thus obtained, the former represents the first cyclic acetal of glycerol to be synthesized containing hydroxyl groups in the alkylidene side chain. It will be observed that they represent the condensation of a simple sugar with a polyhydric alcohol.[8]

The direct condensation of acrolein and ethylene glycol to form acrylidene glycol (2-allyl-1,3-dioxolane) does not take place readily enough to form the basis of a practical method of preparation. The use of catalysts such as anhydrous copper or sodium sulfate, and variation of the experimental conditions, did not appreciably aid the reaction. Catalysts with an acid reaction were precluded due to their action in bringing about a polymerization of the acrolein. Accordingly, the method used was one of indirect synthesis and was an application of that used by Wohl,[9] as modified by Witzemann,[10] for the preparation of open-chain acetals. This slightly modified procedure consisted in dropping acrolein into a solution of hydrogen chloride in ethylene glycol at a temperature of 0 to +5°, the following change taking place.

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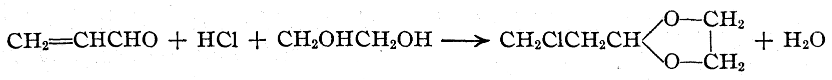
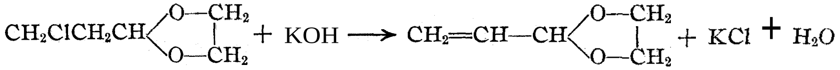
[8] Hydrolysis of this compound should readily yield glyceric aldehyde as one product, although this phase of the subject was not investigated.

[9] Wohl, *Ber.*, **31,** 1797, 2394 (1898); **33,** 3095 (1930).

[10] Witzemann, THIS JOURNAL, **36,** 1766, 1908 (1914).



The reaction mixture was poured into water, the oily layer separated, taken up in ether, dried and fractionated under reduced pressure. The β-chloropropylidene glycol (2-β-chloro-ethyl-1,3-dioxolane) so obtained was heated with dry, powdered potassium hydroxide in order to convert it into acrylidene glycol



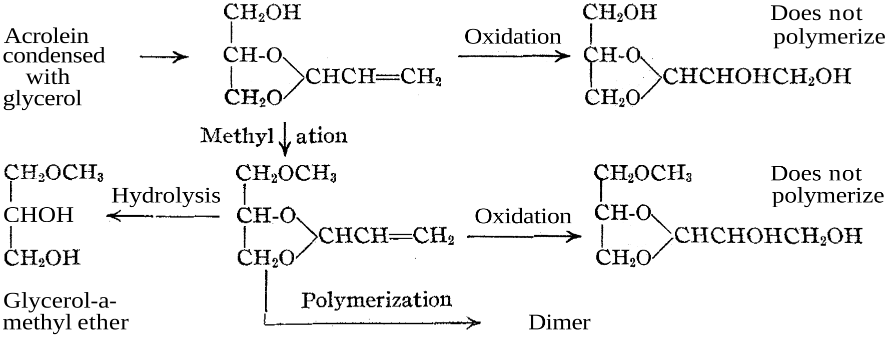
The conversion of acrylidene glycol to 1,2-dihydroxypropylidene glycol (2-dihydroxy-ethyl-l,3-dioxolane) was accomplished by oxidizing with potassium permanganate at a low temperature, removal of the precipitated manganese dioxide, concentration of the slightly alkaline aqueous solution and distillation under low pressure.

Dihydroxypropylidene glycol, as isolated, is a clear liquid with a viscosity approximating to that of ethylene glycol. It burns vigorously when ignited, giving a non-luminous flame. It is quite stable on distillation under reduced pressure and shows no tendency to polymerize under prolonged heating with, or without, non-acid catalysts,

Acrylidene glycerol was prepared by the direct condensation of acrolein and glycerol without a catalyst. The only product isolated from the reaction mixture was shown to possess the five-membered cyclic structure (D) by the usual methylation and hydrolysis technique. No product indicating the presence of the isomeric six-membered acetal could be found. There was always, however, a very large quantity of a thick, viscous, dark brown oil left in the reaction flask, which probably consisted of unchanged glycerol, polyglycerols, polymerized acrolein and possibly a polymerized six-membered cyclic acetal of acrolein and glycerol. No method could be found permitting of the isolation of the individual components.

1,2-Acrylidene-glycerol (2-allyl-1,3-dioxolane-4-carbinol), prepared as above, is a clear liquid of relatively low viscosity, possessing a distinct and somewhat strong odor. It has a marked tendency to hydrolyze, with evolution of acrolein, in dilute aqueous acid solution, especially when warmed. It is monomolecular and shows no tendency toward polymerization. On the other hand, its methyl ether (1,2-acrylidene-glycerol-1′-methyl ether) was found to be a mobile liquid of somewhat pleasant odor, monomolecular when first prepared, but changing after standing for several months into a very viscous product, the composition of which corresponded approximately to that of a dimer. It is possible that this change is due to association, or it may be the result of aggregation involving the migration of a hydrogen atom from one part of the molecule to the double linkage, with subsequent ring closure and polymerization. An interesting comparison is to be found in the fact that acrylic acid ($CH_2=CHCOOH$) shows little or no tendency to polymerize, while with ethyl acrylate ($CH_2=CH—COOC_2H_5$) this tendency is very pronounced.

Both 1,2-acrylidene-glycerol-α-methyl ether and 1,2-acrylidene-glycerol were subjected to oxidation by aqueous permanganate to convert them into the corresponding dihydroxy compounds; thus prepared these were very viscous, high-boiling liquids. They were monomolecular and showed no tendency toward polymerization either under the influence of heat or non-acid catalysts. Distillation of the 1,2-acrylidene-glycerol, however, always left a considerable quantity of a caramel-like, dark brown residue, the nature of which could not be determined. The course of these reactions may be shown as follows



Experimental

Preparation of 8-Chloropropylidene Glycol (2-(β-Chloro-ethyl)-1,3-dioxolane).—Eighty grams of acrolein was allowed to drop slowly, with vigorous stirring, into a solution of 40 g. of hydrogen chloride dissolved in 120 g. of ethylene glycol. The temperature was carefully maintained by means of a freezing mixture at 0 to +4°. If this precaution was not taken the heat of reaction was such that much of the acrolein was polymerized. The reaction mixture was allowed to stand for two hours at room temperature and then poured into a liter of cold water. The β-chloropropylidene glycol separated as an oily layer. It was removed in a separatory funnel, taken up in ether, dried over anhydrous sodium sulfate and fractionated under reduced pressure, yielding 70 g. of a clear, colorless liquid, b. p. 70–72° (18 mm.). A small residue (which was probably polymerized acrolein or β-chloropropionaldehyde) remained in the distillation flask.

β-chloropropylidene glycol on standing gradually turns dark brown in color. When warmed with dilute aqueous acid, a very obnoxious odor, even more offensive than that of acrolein, is evolved, which in all probability is β-chloropropionaldehyde produced by the hydrolysis of the acetal.

Preparation of Acrylidene Glycol (2-Allyl-1,3-dioxolane).—The preparation of acrylidene glycol involved the removal of hydrogen chloride from β-chloropropylidene glycol. Dry powdered potassium hydroxide was used for this purpose.

To six times the theoretical quantity of very finely-powdered potassium hydroxide (124 g.), placed in a round-bottomed copper flask fitted with a short distilling column and condenser, was added 50 g. of β-chloropropylidene glycol. A marked rise in temperature occurred and the mixture was then slowly heated over a free flame until distillation took place. A clear liquid, b. p. 115–119°, was obtained, which on redistillation yielded usually about 20 g. of acrylidene glycol, b. p. 115–116°. Yields from various 50-g. lots averaged approximately 50%.

Excess potassium hydroxide was used in these preparations to absorb the water formed in the reaction. If the latter is allowed to remain uncombined, some of the β-chloropropylidene-glycol undergoes hydrolysis to β-chloropropionaldehyde. A small amount of this compound escapes polymerization by the hot alkali (probably being formed in the vapors above the alkali) and passes over with the distillate giving it an extremely lachrymatory odor, even more pronounced than that of acrolein. Whenever this was formed the yield of acrylidene glycol was always somewhat lower. Acrolein odors were also sometimes present.

If the reaction is carried out in glass flasks great care must be taken to avoid accidents liable to result from the leaking of hot alkali from a cracked flask. For this reason it was found more satisfactory to use a copper vessel.

Acrylidene glycol is a clear, colorless, very mobile and volatile liquid possessing a somewhat strong, sweetish, slightly unpleasant odor. When hydrolyzed by warming with dilute acid, acrolein is readily evolved.

Anal. Calcd. for $C_5H_8O_2$: C, 60.00; H, 8.00. Found: C, 59.28; H, 7.84.

Preparation of **1,2-Dihydroxypropylidene-glycol (2-Dihydroxyethyl-1,3-dioxolane).**—The oxidation of acrylidene glycol to 1,2-dihydroxypropylidene glycol was accomplished by allowing a nearly saturated solution of potassium permanganate to drop into a suspension of acrylidene glycol in water.

Eight hundred and twenty cc. of an aqueous solution containing 42.1 g. of potassium permanganate was added to 40 g. of acrylidene glycol suspended in 400 cc. of water and contained in a three-necked liter flask, the addition being made at the rate of approximately 20 cc. per minute, the mixture being cooled by an ice-bath and vigorously agitated by a mechanical stirrer. The initial temperature was about 9°. After commencement of the reaction the temperature was allowed to fall and then maintained below 5° throughout the addition. The reaction mixture was kept in an ice-bath for two hours, then heated to 90° in a water-bath, the manganese dioxide separated by filtration and the water removed from the aqueous, slightly alkaline filtrate by distillation under reduced pressure at 28° until the volume was approximately 50 cc. The residual liquid was filtered and fractionated; yield, 22 g. (41%) of a viscous, clear, colorless liquid; b. p. 136–138 (5 mm.); n_D^{17} 1.4695.

Anal. Calcd. for $C_5H_{10}O_4$: C, 44.77; H, 7.46. Found: C, 44.38; H, 7.17. Mol. wt. (ethylene bromide). Calcd.: 134. Found: 140.

It is to be noted that the above distillation was carried out using the alkaline solution formed in the oxidation in order to avoid hydrolysis of the acetal.

Preparation of **1,2-Acrylidene-glycerol (2-Allyl-1,3-dioxolane-4-carbinol).**—One hundred and twelve grams (2 moles) of acrolein and 184 g. (2 moles) of glycerol were placed in a pressure bottle and heated for several weeks under pressure at a temperature of 50–60°. Placing the bottle on a warm radiator was found to be satisfactory. On first mixing, the two substances were immiscible, but after heating for several days a homogeneous solution resulted. Various experiments were carried out and it was found that the longer the heating was continued, the better was the yield. The reaction mixture was then distilled under reduced pressure. Usually very little unchanged acrolein remained and the distillate boiling under 165" (10 mm.) was collected separately. A very large quantity of a thick, viscous, undistillable liquid remained which probably contained unchanged glycerol, polyglycerols and various polymerized products. The distillate on fractionation gave a clear oil, b. p. 204–215°; (98–105°, 10 mm.); n_D^{17} 1.4638. It was further refractionated into two fractions, (1) b. p. 204–208°, and (2) b. p. 208–

215°. Both of these reacted as strongly unsaturated substances toward bromine and potassium permanganate, and on warming with dilute acid evolved acrolein very readily. The odor of the fractions when first prepared was marked but not unpleasant; on standing, the odor of acrolein was noticeable due to slight hydrolysis. Yields from a number of experiments averaged between 10 and 15%.

Anal. (Fraction b. p. 98–105°, 10 mm.). Calcd. for $C_6H_{10}O_3$: C, 55.44; H, 7.67. Found: C, 55.40; H, 7.87. Mol. wt. (ethylene bromide). Calcd.: 130. Found: 132.

Determination of Structure.—Both of the above fractions (1) and (2) yielded the same acrylidene-gylcerol-α-methyl ether, the wide range in boiling point possibly being due to the presence of cis and *trans* isomers.

The usual methylation–hydrolysis method was employed and it was found that the acrylidene glycerol as isolated above consisted only of the five-membered acetal. The six-membered acetal either was not formed in sufficient quantity for isolation or it was polymerized and remained in the residue from the reaction.

Methylation of 1,2-Acrylidene-glycerol.—Fifty grams of acrylidene glycerol, b. p. 98–102° (10 mm.), was methylated in the usual manner, using 200 g. of methyl iodide and 120 g. of silver oxide. The reaction mixture was extracted with ether, dried with anhydrous sodium sulfate, and fractionated under reduced pressure; 38 g. of acrylidene-glycerol-a-methyl ether, b. p. 70° (13 mm.), (174–178°, 760 mm.), n_{D}^{17} 1.4408, was obtained. Nine and six-tenths grams of 1,2-acrylidene glycerol, b p. 204–207°, was also recovered.

Acrylidene-glycerol-a-methyl ether is a mobile liquid, monomolecular when first isolated, and possessing a somewhat pleasant, ethereal odor. However, after standing for several months it became very viscous in character and a molecular weight determination showed it had been almost completely converted into a dimer. No hydrolysis had taken place during this period.

Methylation of the other fraction of acrylidene-glycerol, b. p. 208–215°, gave only acrylidene-glycerol-a-methyl ether, b. p. 174–178".

The identity of the material in question was proved by (a) the formation of glycerol-a-methyl ether on hydrolysis, and (b) its conversion into 1,2-dihydroxypropylidene-glycerol-1'-methyl ether on oxidation.

Mol. *wt.* of freshly prepared acrylidene-glycerol-a-methylether in ethylene bromide, calcd.: 144. Found: 145. Mol. *wt.* of above compound after standing (ethylene bromide). Found: 273.

Hydrolysis of Acrylidene-glycerol-α-methyl Ether.—Seven grams of acrylidene-glycerol-a-methyl ether (b. p. 174–178°) was hydrolyzed by boiling under a reflux condenser for seventy minutes with 25 cc. of 75% aqueous ethyl alcohol containing 0.5% hydrochloric acid. Acrolein was evolved vigorously and was removed by applying gentle suction to the top of the condenser. The reaction mixture was neutralized with lead carbonate, filtered, concentrated and the residue distilled under reduced pressure, yielding only glycerol-a-methyl ether, b. p. 110–112° (13 mm.), n_{D}^{17} 1.4465, and thus serving to identify the structure of the original product as the five-membered acrylidene glycerol, (D).

Preparation of 1,2-Dihydroxypropylidene-glycerol-1'-methyl Ether.—The simplest and most dependable mode of synthesis appeared to lie in the oxidation of acrylidene-glycerol-a-methyl ether to the corresponding dihydroxy compound. By protecting the a-hydroxyl group by a prior methylation, it was thought that any secondary oxidation might be avoided. Moreover, this would yield a new type of cyclic acetal ether.

Thirty grams of acrylidene-glycerol-a-methyl ether was suspended in 300 cc. of water and oxidized in the usual manner with 560 cc. of an aqueous solution containing 29.5 g. of potassium permanganate. The water was removed from the filtered, slightly alkaline solution by distillation under reduced pressure. The residual oil on fractionation and refractionation yielded 9.4 g. of a heavy, slightly yellowish liquid, b. p. 146° (1–2 mm.), n_D^{17} 1.4680. Analysis showed it to be 1,2-dihydroxypropylidene-glycerol-1'-methyl ether.

Anal. Calcd. for $C_7H_{14}O_5$: C, 46.54; H, 7.92. Found: C, 46.56; H, 7.98. Mol. wt. (ethylene bromide). Calcd.: 178. Found: 197.

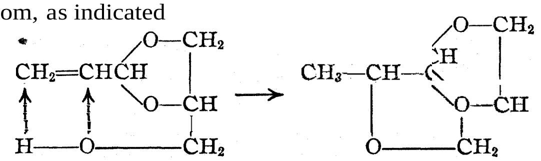
The product shows no tendency to polymerize either on heating or under the influence of non-acid catalysts such as alkalies, aluminum alkylates, etc.

Synthesis of **1,2-Dihydroxypropylidene-glycerol (1,2) (1,2-Dihydroxy-ethyl-1,3-dioxolane-4-carbinol)**.—Twenty-five and five-tenths grams of 1,2-acrylidene-glycerol (b. p. 204–207°) was dissolved in 250 cc. of water and oxidized with a solution containing 20.7 g. of potassium permanganate in 365 cc. of water under the same conditions that were employed in the preceding experiment. The reaction product after filtration, but without neutralizing, was concentrated under reduced pressure. The residual oil on fractionation yielded 3 fractions—(1) 8 g. of a clear oil, b. p. 54° (2 mm.); (2) a small quantity of unchanged acrylidene-glycerol, b. p. 70° (2 mm.); and (3) 28 cc. of a very viscous, slightly yellow-colored liquid, b. p. 200–204° (6 mm.), n_D^{17} 1.4888, proved by analysis to be 1,2-dihydroxypropylidene-glycerol (1,2-) and which could be redistilled unchanged. A large, undistillable, tarry, caramel-like residue remained.

The identity of Fraction I, b. p. 54° (2 mm.), was not determined. It behaved as a saturated substance toward potassium permanganate and bromine and also reacted with metallic sodium. On warming with dilute acid an aldehyde was evolved, the identity of which was not determined.

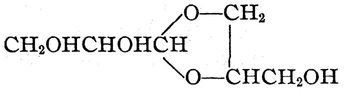
Anal. of Fraction (3). Calcd. for $C_6H_{10}O_3$: C, 55.44; H, 7.67. Mol. wt., 130. Found: C, 55.40; H, 8.00. Mol. wt. (ethylene bromide), 124.

It is possible that the product represents a bicyclic acetal formed by the wandering of a hydrogen atom, as indicated



The product is at present under investigation. If this mechanism should prove correct, the reaction would form an interesting example of the wandering of a hydrogen atom to a vinyl radical in an *alkaline* medium.

1,2-Dihydroxypropylidene-glycerol (1,2),



$$CH_2OHCHOHCH\begin{cases}O-CH_2\\O-CHCH_2OH\end{cases}$$

—1,2-Dihydroxypropylidene-glycerol-1,2 is monomolecular, and as far as could be determined, shows no tendency to polymerize on heating with, or without, non-acid catalysts. During its preparation a large quantity of residue remained and it was thought that a better yield could be obtained by carrying out the distillation at a very low pressure. However, distillation at 0.15 mm. (using a Hyvac and mercury vapor pump) gave no better results, the reaction product yielding only 2 g. of dihydroxypropylidene-glycerol (1,2), b. p. 146" (0.15 mm.). A considerable amount of a caramel-like substance again remained but it was impossible to determine whether this represented a polymerization or a decomposition product.

Anal. of 1,2-Dihydroxypropylidene-glycerol (1,2). Calcd. for $C_6H_{12}O_5$: C, 44.77; H, 7.46; mol. wt. 163. Found: C, 44.38; H, 7.17; mol. wt. (acetone), 156.

Attempts to Bring about Polymerization.—1,2-Dihydroxypropylidene-glycerol

(1,2) was heated for several weeks at 110° with non-acid catalysts such as potassium hydroxide, and sodium and aluminum ethylates, but no tendency to polymerize was observed. Likewise, heating for long periods at 110° without a catalyst, or exposure to sunlight in a quartz glass tube, had no effect.

The close relationship of 1,2-dihydroxypropylidene-glycerol (1,2) to the cellulose nucleus was previously pointed out,[3] and it would seem that polymerization does not take place unless ring closure has been previously effected.

Summary

1. Two new unsaturated cyclic acetals, namely, acrylidene-glycol and acrylidene-glycerol have been prepared. Their physical properties and chemical behavior have been investigated.
2. It is shown that the reaction product from the condensation of acrolein and glycerol yields a five-membered acrylidene glycerol. The greater part of the reaction product is left as a thick, viscous residue. No indication was observed of the presence of the corresponding six-membered acetal, although it is possible that it may be formed and at once undergo spontaneous polymerization.
3. The corresponding acrylidene-glycerol methyl'ether was prepared. It undergoes polymerization to a dimolecular form on standing.
4. The dihydroxypropylidene cyclic acetals of glycol and glycerol were prepared and their properties studied. They are apparently the first cyclic acetals of glycol and glycerol that have been prepared containing hydroxyl groups in the alkylidene radical.
5. Dihydroxypropylidene glycol and glycerol as well as dihydroxy-propylidene-glycerol-a-methyl ether show no tendency to polymerize, a fact of some interest in connection with their relationship to cellulose and other polysaccharides.

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SOME OBSERVATIONS ON THE ACETOACETIC ESTER CONDENSATION

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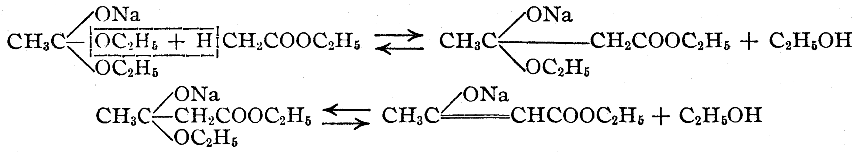
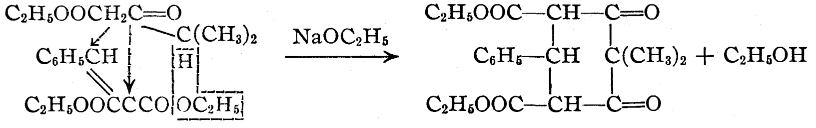
The well-known mechanism for the course of the acetoacetic ester condensation proposed by Claisen[1] was questioned by Dieckmann[2] on the basis of his work on the splitting of alkyl acetoacetic esters by alcohol and sodium ethoxide. Dieckmann preferred to represent the condensation as a reversible reaction that took place in two phases



$$CH_3\overset{ONa}{\underset{OC_2H_5}{C}}-\boxed{OC_2H_5 + H}CH_2COOC_2H_5 \rightleftarrows CH_3\overset{ONa}{\underset{OC_2H_5}{C}}-CH_2COOC_2H_5 + C_2H_5OH$$

$$CH_3\overset{ONa}{\underset{OC_2H_5}{C}}-CH_2COOC_2H_5 \rightleftarrows CH_3\overset{ONa}{C}=CHCOOC_2H_5 + C_2H_5OH$$

According to this explanation it is necessary to have only one hydrogen atom on the a-carbon atom of the ester that condenses with the ortho derivative in order to bring about the first phase of the condensation. The reason for the apparent failure of an ester of the type, $R_2CHCOOC_2H_5$, to undergo the acetoacetic ester condensation is due, according to Dieckmann, to the ease with which the condensation product is split, *i. e.*, the relative completeness of the reversal of the first phase of the above reaction. In support of this mechanism Dieckmann and Kron[3] reported the condensation of ethyl *iso*butyryl acetate and benzalmalonic ester by means of sodium in absolute alcohol to 2,2-dimethyl-5-phenyl-4,6-dicarbethoxycyclohexandedione-1,3



The enolic acidity of the condensation product resulting from the simultaneous formation of two β-ketonic ester groupings prevented the reversal of the acetoacetic ester condensation.

In 1922 Scheibler and Ziegner[4] proposed a new mechanism, which resembled that of Dieckmann's to the extent that it indicated that esters of the type $R_2CHCOOC_2H_5$ should undergo the condensation. This new proposal, however, met with considerable criticism[5] and was recently

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[1] Claisen, Ber., 20, 651 (1887); *ibid.*, **21**, 1154 (1888).

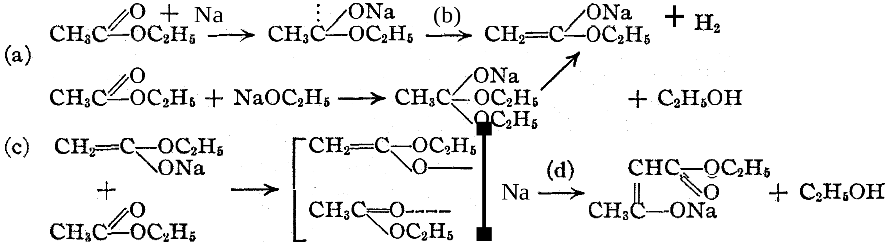
[2] Dieckmann, *ibid.*, **33**, 2678 (1900).

[3] Dieckmann and Kron, *ibid.*, **41**, 1260 (3908).

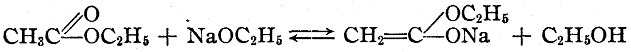
[4] Scheibler and Ziegner, *ibid.*, **55**, 789 (1922).

[5] Adickes, *ibid* , 59, 2522 (1926); *ibid.*, 60, 272 (1927); Franklin and Short, *J. Chem. Soc.*, 591 (1928).

abandoned by Scheibler and Marhenkel[6] in favor of a rather complicated formulation which assumes four phases in the condensation: (a) the formation of a metal ketyl (when a metal such as sodium is used) or an addition product (when a metallic alkoxide is used) on the ester carbonyl group; (b) the change of the compound formed in (a) into an enolate; *(c)* reaction of the enolate with a molecule of the keto form of the ester with the formation of a molecular compound; (d) the formation of a condensation product from the molecular compound formed in (c) by splitting out alcohol. To illustrate with ethyl acetate, sodium and sodium ethoxide



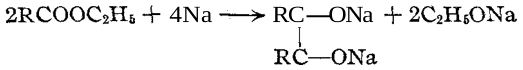
This mechanism resembles Claisen's original proposal to the extent that for complete condensation two hydrogen atoms are required on the α-carbon atom of the ester molecule that reacts with the keto form. Scheibler and Marhenkel state that when sodium ethoxide is the condensing agent, it is the alcohol split out when the enolate is formed (b) that prevents the continuation of the reaction; in other words, the ester enolate is a necessary intermediate and the reversible phase of the acetoacetic ester condensation is



$$CH_3C(=O)OC_2H_5 + NaOC_2H_5 \rightleftharpoons CH_2{=}C(OC_2H_5)ONa + C_2H_5OH$$

They state further that an ester of the type $R_2CHCOOC_2H_5$ will proceed in the above transformations through phase (c) but cannot go through phase (d) for obvious structural reasons. This conclusion is based on their observation that such an ester forms with sodium ethoxide **a** ketene acetal.

In the application of the acetoacetic ester condensation to ethyl acetate and its higher homologs, the choice between sodium and sodium ethoxide as condensing agents is an important consideration. It has been shown[7] that such esters in ether solution react with sodium at 0° to form sodium derivatives of acyloins



$$2RCOOC_2H_5 + 4Na \longrightarrow \begin{array}{l} RC{-}ONa \\ \;| \\ RC{-}ONa \end{array} + 2C_2H_5ONa$$

This reaction is quite distinct from the acetoacetic ester condensation and in no way involves the hydrogens of the a-carbon atom of the ester

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[6] Scheibler and Marhenkel, Ann., 458, 1 (1927).

[7] Bouveault and co-workers, Bull. *soc. chim.*, 35, 629 (1906), and preceding papers.

because it will proceed when R is tertiary butyl. Work now in progress in this Laboratory and which will be the subject of a future communication indicates that this competing reaction takes place at higher temperatures than 0° and that the acyloin type may be the major if not the sole product of the reaction between esters of this type and sodium.

In order to avoid this complication sodium ethoxide was used as a condensing agent in the work reported here. It seemed that the difficulty of the reversal of the condensation (which Dieckmann[2] has shown to be more serious with alkyl acetoacetic esters than with the unsubstituted ester) could be overcome by the removal of the alcohol by distillation as it was formed in the reaction. This principle has been applied[8] to the large scale production of acetoacetic ester from ethyl acetate using sodium, potassium or magnesium as condensing agents.

In the procedure that was used in the present work the ester was allowed to react with sodium ethoxide, the reaction mixture periodically distilled and the distillate replaced with pure ester. The amount of alcohol formed in the reaction was determined from the refractive indices of the distillates and when it was indicated that no more alcohol was being formed, the β-keto-ester was isolated from the reaction mixture.

Ethyl acetate, ethyl propionate, ethyl butyrate and ethyl *iso*butyrate were treated in this manner. Since a large excess of ester was necessarily taken, the yield calculations were based on the amount of sodium ethoxide used, according to the equation

$$2RCH_2COOC_2H_5 + NaOC_2H_5 = RCH_2C(ONa)CRCOOC_2H_5 + 2C_2H_5OH$$

The yields of β-keto-esters and of alcohol obtained from these various esters, using 0.5 mole (34 g.) of sodium ethoxide as the condensing agent are summarized in Table I.

TABLE I

YIELDS OF β-KETO-ESTERS

Ester used	Condensation product	Keto-ester isolated Mole	% of theoretical	Alcohol in distillate Mole	% of theoretical
Ethyl acetate	Ethyl acetoacetate	0.340	68	0.83	**83**
Ethyl propionate	Ethyl a-propionylpropionate	.405	81	0.97	97
Ethyl butyrate	Ethyl a-butyrylbutyrate	.380	76	1.03	103
Ethyl isobutyrate	....		0	0.03"	6[a]

[a] In this case the theoretical yield of alcohol would be 0.5 mole instead of 1 mole as is the case with the other esters under consideration.

While under ideal conditions the percentage yield of alcohol should be the same as that of the β-keto-ester in each case, the discrepancy between the two that is shown in the above table is not particularly great when manipulative losses during the isolation of the keto-ester, effect of traces of water on the yield of alcohol ($1H_2O$ produces $2C_2H_5OH$), possible im-

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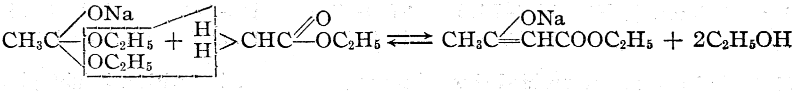
[8] U. S. **Patent** 1,472,324; reissue 16,591.

purities in the sodium ethoxide, and the method of analysis for alcohol in the distillates are considered, The results show that the reversal of the condensation can be prevented by such a procedure, since Higley[9] has found that the equilibrium point in the acetoacetic ester condensation represents about 36% of the keto-ester and the work of Dieckmann[2] indicates that a still smaller percentage of keto-ester would be present at the equilibrium point of alkyl-substituted acetoacetic esters.

The results obtained with ethyl isobutyrate are of some interest in connection with the mechanisms that have been proposed for the condensation. It is seen that no keto-ester and an insignificant amount of alcohol are formed in the reaction of this ester with sodium ethoxide. If Dieckmann's proposal were correct, it is difficult to see why this ester under the conditions of the experiment should not condense to form the sodium ethoxide addition compound of ethyl isobutyryl-isobutyrate, $(CH_3)_2C(ONa)(OC_2H_5)C(CH_3)_2COOC_2H_5$, with the simultaneous appearance of alcohol in the distillate, for this keto-ester is known[10] to be sufficiently stable to isolate. Both Claisen's original proposal and Scheibler's later suggestion as to the mechanism of the reaction are in accord with the fact that none of the β-keto-ester is formed from ethyl isobutyrate, but Scheibler's postulate that an intermediate enolate is an essential step in the course of the reaction is not in agreement with the fact that no alcohol is found in the distillate.

It seems on the basis of these results that the original mechanism for the acetoacetic ester condensation proposed by Claisen, supplemented by the reversible feature



$$CH_3C\begin{matrix}\diagup ONa \\ - OC_2H_5 \\ \diagdown OC_2H_5\end{matrix} + \begin{matrix}H \\ H\end{matrix}>CHC\begin{matrix}\diagup\!\!\diagup O \\ - OC_2H_5\end{matrix} \rightleftharpoons CH_3C\overset{ONa}{=}CHCOOC_2H_5 + 2C_2H_5OH$$

is the most acceptable of those that have been considered. It may be suggested that the results presented here do not prove conclusively the correctness of the Claisen mechanism, but rather that they support it to the extent that they do not show it to be incorrect. The behavior of ethyl isobutyrate does show, however, that the mechanisms proposed by Dieckmann and by Scheibler and Marhenkel for the reaction of sodium ethoxide and esters of the type of ethyl acetate are questionable.

Since Scheibler and Marhenkel postulate the same enolate (b) and molecular compound (c) as necessary precursors for both the acetoacetic ester condensation and ketene acetal formation it appears that their mechanism for the formation of the latter type is also in error. The ketene acetal from ethyl isobutyrate has been prepared[11] by the action

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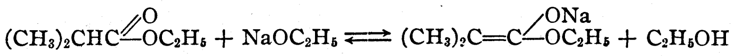
[9] Higley, *Am. Chem.* J., *37, 299* (1907).

[10] Salkind, *Chem. Centr.,* II, *315 (1906).*

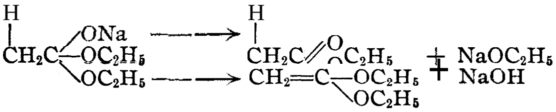
[11] Scheibler and Friese, *Ann., 445, 149 (1926).*

of sodium ethoxide on this ester, but it has been pointed out above that these two reactants do not enter into the reversible reaction



$$(CH_3)_2CHC\overset{\diagup O}{—}OC_2H_5 + NaOC_2H_5 \rightleftharpoons (CH_3)_2C{=}C\overset{\diagup ONa}{—}OC_2H_5 + C_2H_5OH$$

which is essential to the Scheibler and Marhenkel mechanism. For this reason it seems that a different explanation for the formation of ketene acetals is needed. In this connection it may be suggested that it would not be unreasonable to assume that Claisen's ester–sodium ethoxide addition product might undergo decomposition in two ways, (a) into the original ester and sodium ethoxide and (b) into a ketene acetal and sodium hydroxide, e. g.



Experimental

Materials Used.—–Each of the esters, ethyl acetate, ethyl propionate, ethyl butyrate and ethyl isobutyrate, that was used was purified in the following manner. The ester was shaken in a separatory funnel with an equal volume of 2% potassium carbonate solution and then with an equal volume of water. The ester layer was separated and allowed to stand for three days over anhydrous potassium carbonate, after which it was filtered and distilled. The distillate was treated with 2% of its weight of phosphorus pentoxide and after standing for twenty-four hours it was distilled from the phosphorus pentoxide. The distillate was then fractionally distilled The boiling points and refractive indices of the esters used in the experiments described below were:

Ethyl ester	Acetate	Propionate	Butyrate	Isobutyrate
B. p. (735 mm.), °C.	76.4–76.5	97.5–98.4	119–121	108.5–109.5
n_D^{25}	1.36899	1.38053	1.38883	1.38404

The ethyl acetate so purified showed no apparent reaction with a bright piece of sodium after six hours. The ethyl propionate showed a slight reaction after about one hour. The ethyl butyrate and ethyl isobutyrate reacted completely with sodium (acyloin formation) within a few minutes. In no case, however, was there any evidence of evolution of hydrogen. Although it has been pointed out[12] that the distillation of ethyl acetate from phosphorus pentoxide caused a slight amount of decomposition, as indicated by a change in density of the ester, it was felt that the decomposition induced by this treatment was not sufficient to have any marked effect on the results of this work.

The sodium ethoxide that was used was prepared by dissolving freshly cut sodium in absolute alcohol (distilled from sodium) and, while the final hydrogen was being evolved from the reaction, removing the excess alcohol by distillation. The resultant sodium ethoxide was then heated in an oil-bath to 150° at 20 mm. for four hours.

Determination of Alcohol in the Ester Distillates.—Mixtures of varying percentages of the different esters and absolute alcohol were made up, their refractive indices taken, and these values plotted against the percentage composition. The points thus determined did not fall on the line joining the refractive index of the pure ester and that of pure alcohol (n_D^{25} 1.35774) but formed a smooth curve, quite dose to this line, of the

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[12] Wade and Merriman, *J. Chem. Soc.*, 101, 2429 (1912).

type recently reported by Adkins and Broderick[13] for mixtures of different aldehydes and alcohols. Within the range used (80–100% ester) for the analyses of the distillates the greatest difference between the refractive indices as given by the curve and the straight line amounted to only 0.0004. In spite of this small difference the curves obtained from mixtures of ester and alcohol of known composition and their corresponding refractive indices were used for the analyses. The refractive indices were determined with a Pulfrich refractometer at 25° and with an accuracy, it is believed, of 0.0001.

Reaction of the Esters with **Sodium Ethoxide.**—The standard procedure that was used for all of the esters with the exception of ethyl isobutyrate was: 280 g. of the ester and 34 g. (0.5 mole) of sodium ethoxide were placed in a 1-liter three-necked flask fitted with a reflux condenser, a mercury seal stirrer and a condenser for downward distillation. The receiver to this latter condenser was arranged to fit tightly or loosely depending on whether it was desired to send the vapors of the boiling reaction mixture into the reflux condenser or through the other condenser for distillation. All connections in the apparatus were ground-glass joints in order to prevent any contamination from stoppers. The top of the reflux condenser carried a calcium chloride tube. The contents of the flask was refluxed for four hours, with stirring, by heating in an oil-bath. After this time the excess ester was distilled off and collected in two portions (1 and 2, Table II). Then 200 g. of pure ester was added to the reaction flask and the mixture allowed to reflux for three hours. After this time the excess ester was again distilled off and collected in two portions (3 and 4, Table II). Finally 100 g. of pure ester was added to the flask and after allowing it to reflux for three hours it was distilled off and collected in one portion (5, Table II).

In the case of ethyl isobutyrate a similar procedure was followed except that after the four-hour period of refluxing of 0.5 mole of sodium ethoxide and 280 g. of the ester, the distillation was carried on slowly over a period of three hours. The distillate was

TABLE II

SUMMARY OF EXPERIMENTAL DATA

	Portion	Weight, g.		C_2H_5OH, %	C_2H_5OH, g.	
Ethyl acetate	1	104.0	1.36699	17	17.7	Total, 38.5 g. (0.83 mole)
	2	75.0	1.36726		11.2	
	3	79.0	1.36835		7.6	
	4	102.0	1.36881	2	2	
	5	153.0	1.36909	0	0	
Ethyl propionate	1	108.0	1.37649	17	18.3	Total, 44.9 g. (0.97 mole)
	2	85.5	1.37676	16	13.6	
	3	14.5	1.37846	9	10.2	
	4	71.5	1.37967	4	2.8	
	5	103.5	1.38045	0	0	
Ethyl butyrate	1	171.5	1.38291	18	30.8	Total, 47.3 g. (1.03 mole)
	2	54.0	1.38567	10	5.4	
	3	74.5	1.38663	7	5.2	
	4	98.5	1.38709	6	5.9	
	5	71.0	1.38892	0	0	
Ethyl isobutyrate	1	52.3	1.38326	3	1.5	Total, 1.5 g. (0.03 mole)
	2	64.3	1.38405	0	0	
	3	30.0	1.38405	0	0	
	4	51.2	1.38405	0	0	

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[13] Adkins and Broderick, THIS JOURNAL, 50, 499 (1928).

collected in four portions. Due to the fact that practically no alcohol appeared in the distillate and that the boiling point of the latter was identical with that of the pure ester, no fresh portions of the ester were added to the reaction flask.

A summary of the weights, refractive indices and alcohol content of the distillate portions for the different esters used is shown in Table II.

The condensation product was isolated from the residue in the reaction flask by the addition, with constant cooling and stirring, of a solution of 35 g. of glacial acetic acid in 70 cc. of water. When complete solution of the salt had taken place, the ester layer was separated and the aqueous portion extracted with two 50-cc. portions of ether. The combined ester layer and ether extract was then fractionated. In this manner there were obtained 44 g. of ethyl acetoacetate (68% of calcd.), b. p. 78–80" (16 mm.); 64 g. of ethyl a-propionylpropionate (81% of calcd.), b. p. 88–90" (12 mm.); 70 g. of ethyl α-butyrylbutyrate (76% of calcd.), b. p. 102–105° (12 mm.). All yield calculations were based on the amount of sodium ethoxide used. The two latter compounds were definitely characterized by hydrolysis to diethyl ketone and di-n-propyl ketone, the semicarbazones of which melted at 139–140° and 133–134°, respectively.[14] In the case of ethyl isobutyrate this ester was the highest boiling product that was isolated from the reaction mixture.

Ethyl a-propionylpropionate has been prepared in rather poor yields by the action of sodium on ethyl propiouate[15] Although ethyl a-butyrylbutyrate has previously been prepared,[16] it has not heretofore been prepared by a Claisen condensation of ethyl butyrate.

Summary

1. A study of the action of sodium ethoxide on ethyl acetate and certain of its higher homologs has been made and the amounts of both reaction products, β-keto-ester and alcohol, that were formed have been determined.

2. Certain of the mechanisms that have been proposed for the course of the acetoacetic ester condensation are discussed in the light of the results which have been obtained.

MADISON, WISCONSIN

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[14] Cf. Haehn, *Ber.*, **39**, 1703 (1906).

[15] Israel, Ann., **231**, 198 (1886); Hantzsch and Wohlbruck, ***Brr.***, 20, 1320 (1837).

[16] Beilstein, "Handbuch der organischen Chemie," **1921**, Vol. III, p. 706.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE RICE INSTITUTE]

ALPHA-FURFURYL CHLORIDE AND ITS DERIVATIVES. II

BY W. R. KIRNER AND G. HOLMES RICHTER

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The recent preparation and isolation of α-furfuryl chloride[1] has greatly simplified the synthesis of a-furfuryl compounds and it is now possible, by using this reagent, to prepare compounds which were in many cases previously obtainable only by more or less indirect methods which usually started with furfural and involved several steps in the procedure. By the use of a-furfuryl chloride, which contains a highly reactive chlorine atom, we have prepared the following new compounds, which are listed in Table I, together with their physical constants.

TABLE I

NEW FURYL DERIVATIVES

No.	Name	B. p., °C.	Press., mm.	M. p., °C.	Yield, %	d_4^{20}	n_D^{20} (Abbé)	Molecular refraction Calcd.	Molecular refraction Obs.
1	Ethyl a-furfurylmalonic ester	135.5–136.5°	5	....	67	.....	....	....	....
2	Ethyl a-furfurylbarbituric acid	....	..	144.5–145	51	.....	....	....	....
3	a-Furfuryl-acetoacetic ester	111–111.5°	4	....	61	1.10366	1.4718	53.172	53.290
4	a-Furfuryl nitrile	74–75°	27	....	90	1.04627	1.4833	30.571	29.236
5	a-Furylacetic acid	....	..	108.5–109.5	43	.....	....	....	....
6	a-Furfuryl thiocyanate	111.5–112.5°	27	....	70	1.18709	1.5614	36.083	37.971
7	a-Furfuryl ethyl sulfide	90.5–91°	28	....	80	1.04958	1.5140	41.005	40.773

We have also prepared the following known substances (Table II) by simple replacement reactions, whereas their previous preparation started with furfural and was accomplished by more or less roundabout methods.

TABLE II

SUBSTANCES PREPARED

No.	Name	B. p.. °C.	Press., mm.
1	a-Furfurylmalonic ester	125.5–127	4
2	α-Furfurylbarbituric acid	....	..
3	2-α-Furfurylacetic acid	....	..
4	a-Furfuryl acetone	....	..
5	a-Furfuryl acetone semicarbazone	....	..
6	α-Furfuryl mercaptan	84	65

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[1] Kirner, THIS JOURNAL, **50,** 1955 (1928).

TABLE II (Concluded)

No.	M p., °C.	Yield, %	d_4^{20}	n_D^{20} (Abbé)	Molecular refraction Calcd.	Obs.
1	....	76	1,10999	1.4591	59.433	59.152
2	186–187.5	37	.....	....	....	....
3	56.5–58	75	.....	....	....	....
4	....	12	.....	....	....	....
5	140–141	..	.....	....	....	....
6	....	33	1.13186	1.5329	31.489	31.302

In most of these reactions it was not considered necessary to use the pure distilled furfuryl chloride so the ethereal solution obtained directly from the reaction mixture was treated with the desired reagent. The main objection to this procedure is that it does not permit of an accurate method of determining the yield of product theoretically obtained in the various reactions. However, by assuming that the crude reaction product was formed in 70% yield (since a 63% yield of distilled product can be obtained), an approximate idea is obtained of the percentage yields in the various reactions.

The furfuryl-ethyl-barbituric acid is of special interest because of the possibility of its possessing a physiological activity analogous to that of Veronal. We are indebted to Professor A. M. Hjort of the Dartmouth Medical School for his investigation of the action of this substance in producing hypnosis. A more detailed report of the physiological action will be published elsewhere.

Experimental

α-Furfurylmalonic Ester.—This substance was first prepared by Sandelin[2] by condensing furfural with malonic acid, yielding furfuralmalonic acid which was then reduced to furfurylmalonic acid and esterified; b. p. 171–173° at 33 mm.; 265–267° at atmospheric pressure. It was described as a light yellow oil with a weak fruity odor. This ester was also prepared by Ojiyama, Hasegawa and Matsumura.[3] Only the abstract of their article was available in which no details were given but their method is obviously complicated.

We obtained this ester by the usual malonic ester condensation using thoroughly anhydrous alcohol prepared according to the method of Smith[4] In this one case distilled furfuryl chloride was used and was added in a solution of Grignard ether. The yield of distilled product was 76%; b. p. 125.5–127° at 4 mm. The product was a colorless oil with an odor resembling that of malonic ester; d_{20}^{20} 1.11196; d_4^{20} 1.10999; n_D^{20} 1.4591; M_D (calcd.) 59.433; M_D (obs.) 59.152.

Anal. Subs., 0.2033: CO_2, 0.4457; H_2O, 0.1283. Calcd. for $C_{12}H_{16}O_5$: C, 59.98; H, 6.72. Found: C, 59.79; H, 7.06.

Ethyl-α-furfurylmalonic Ester.—This is a new compound. It was made by ethylating the above furfurylmalonic ester in the usual manner using ethyl iodide. The

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[2] Sandelin, Ber., 33, 490 (1900).

[3] Ojiyama, Hasegawa and Matsumura, J. *Pharm. Soc.* Japan, 533, 597 (1926); C. A., 21,2251 (1927).

[4] Smith, J. *Chem. Soc.*, 1288 (1927).

purification of the compound was found difficult due to the continued appearance of iodine during the vacuum distillation. This was finally all removed by several extractions with sodium thiosulfate solution. The boiling point was 135.5–136.5° at 5 mm.; yield, 67%. This substance was not analyzed but was used directly for the preparation of the furfuryl-ethylbarbituric acid.

α-Furfurylbarbituric Acid.—This substance was first prepared by Ojiyama, Hasegawa and Matsumura.[3] They gave the melting point as 193°. We prepared it according to the directions given by Dox and Yoder,[5] using furfurylmalonicester, urea and sodium ethylate made from special anhydrous alcohol. In the isolation of the compound it was found that it was quite sensitive to the action of mineral acids and therefore should be left in contact with them over as short a period as possible and at a low temperature. The yield was 37%; m. p. 186–187.5°.

Anal. Subs., 0.2511: N_2, 30.00 cc. at 26° and 762.3 mm. Calcd. for $C_9H_8O_4N_2$: N, 13.46. Found: N, 13.53.

Ethyl-α-furfurylbarbituric Acid.—This is a new compound and was made in precisely the same manner as the substance just described above; yield, 51%; m. p. 144.5–145°.

Anal. Subs., 0.1168: N_2, 13.15 cc. at 23.6° and 760.1 mm. Calcd. for $C_{11}H_{12}O_4N_2$: N, 11.86. Found: N, 12.41.

α-Furfurylacetoacetic Ester.—This new substance was prepared by the usual acetoacetic ester condensation using specially dehydrated alcohol, the crude furfuryl chloride being added in a solution of dry ether. The product was purified by distillation in a vacuum; b. p. 111.0–111.5° at 4 mm.; yield, 61%; d^{20}_{20} 1.10562; d^{20}_{4} 1.10366; n^{20}_{D} 1.4718; M_D (calcd.) 53.172; M_D (obs.) 53.290.

Anal. Subs., 0.1993: CO_2, 0.4556; H_2O, 0.1193. Calcd. for $C_{11}H_{14}O_4$: C, 62.83; H, 6.71. Found: C, 62.34; H, 6.70.

2-α-Furfurylacetic Acid (3-α-Furylpropanoic Acid).—Baeyer[6] and also Marckwald[7] made this acid by first carrying out a Perkin's synthesis on furfural, yielding furfurylacrylic acid, which was then reduced. They give the melting point as 50–51°. Marckwald[8] also obtained it by preparing furfurylmalonic acid, which was heated and thus made to lose carbon dioxide. Sandelin[9] prepared furfuralmalonic ester, which was converted to furylsuccinic acid; this on loss of carbon dioxide yielded the furfurylacetic acid. He gave the melting point as 58.5°.

We obtained this acid by the usual acid splitting of the acetoacetic ester using very concentrated alkali for the hydrolysis according to the conditions given by v. Euler and Ölander.[10] We obtained in this way a 75% yield of crude product which was twice recrystallized from water; m. p. 56.5–58°.

α-Furfurylacetone (1-α-Furylbutanone-3).—This substance has been made by carrying out a Claisen condensation between furfural and acetone, yielding furfuralacetone, which on reduction with sodium amalgam gives the saturated ketone.[11] We obtained the ketone as a by-product in the acid splitting of the acetoacetic ester;

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[5] Dox and Yoder, THIS JOURNAL, **44**, 1141 (1922).

[6] Baeyer, *Ber.*, **10**, 357 (1877).

[7] Marckwald, *ibid.*, **20**, 2812 (1887).

[8] Marckwald, *ibid.*, **21**, 1083 (1888).

[9] Sandelin, *ibid.*, **31**, 1122 (1898).

[10] v. Euler and Ölander, *Z. anorg. Chem.*, **147**, 304 (1925).

[11] Harries and Kaiser, *Ber.*, **32**, 1320 (1899); Fujita, *J. Pharm. Soc. Japan*, **519**, 456 (1925); *C. A.*, **20**, 412 (1926); Kasiwagi, *Bull. Chem. Soc. Japan*, *1*, 90 (1926); *C. A.*, *20*, 3005 (1926).

yield of crude product, 12%. It was converted into the semicarbazone which melted at 140–141°. Harries gave the melting point as 143".

a-Furfuryl Nitrile.—This is a new compound. It was prepared by treating a very concentrated aqueous solution of sodium cyanide dropwise with furfuryl chloride, the mixture being heated to about 70°. When the addition was complete, the mixture was heated just to the boiling point and cooled. Two layers separated. The oily layer was removed, the aqueous solution extracted with ether and the combined layers dried over anhydrous sodium sulfate. The crude yield was 90%. It was found difficult to obtain the compound in a pure state. Four systematic vacuum fractionations were carried out, yielding a colorless liquid possessing a very sweet odor; b. p. 74–75" at 27 mm.; d_{20}^{20} 1.04813; d_4^{20} 1.04627; n_D^{20} 1.4833; M_D (calcd.) 30.571; M_D (obs) 29.236.

Anal. Subs., 0.1528: N_2, 16.82 cc. at 765.3 mm. and 25". Calcd. for C_6H_5ON: N, 13.08. Found: N, 12.57.

a-Furylacetic Acid.—This new acid was obtained by hydrolyzing the above nitrile using a 25% solution of potassium hydroxide. The hydrolysis went rapidly after heating the mixture for only four to five minutes, the oily layer disappearing; heating was continued for one hour. The alkaline solution was extracted with ether to remove unhydrolyzed impurities, then cooled to 10°, decolorized and filtered. The filtrate was treated with excess concentrated hydrochloric acid; crystallization of the acid started immediately on cooling; yield, 43%; m. p. 108.5–109.5".

Anal. Subs., 0.1813: CO_2, 0.3802; I-120, 0.0776. Calcd for $C_6H_6O_3$: C, 57 13; H, 4.80. Found: C, 57.19; H, 4.79.

α-Furfuryl Thiocyanate.—This new substance was prepared by treating furfuryl chloride with sodium thiocyanate in acetone solution, a method suggested by the work of Steinkopf, Herold and Stöhr.[12] Sodium chloride precipitated immediately and the mixture was refluxed for two and one-half hours and allowed to stand overnight. The product was isolated by filtering, adding water, extracting with ether and then drying the ethereal solution over anhydrous sodium sulfate Distillation in a vacuum yielded a colorless oil boiling at 111.5–112.5° at 27 mm.; yield, 70%; b. p. (2 mm.) 66–67'; d_{20}^{20} 1.18919; d_4^{20} 1.18709; n_D^{20} 1.5614; M_D (calcd. as RSCN) 36 083; M_D (obs.) 37.971.

Anal. Subs., 0.1998: $BaSO_4$, 0.3350. Calcd. for C_6H_5OSN: S, 23.04. Found: S. 23.03.

α-Furfuryl Mercaptan.—The only previous preparation of this compound which could be found in the literature was given in a patent issued to Staudinger and Reichstein.[13] Since only the abstract was available no details of the preparation could be learned except that furfural was converted into *bis*-furfuryl disulfide by treatment of furfural with ammonium hydrosulfide which was then reduced to the mercaptan. No physical properties of the compound were given.

The first synthesis attempted was the treatment of furfuryl chloride with sodium hydrosulfide; this was unsuccessful. The mercaptan was finally obtained by first condensing furfuryl chloride with thiourea and then hydrolyzing this product, without isolating it, to the mercaptan. After hydrolysis the mercaptan was extracted with carbon tetrachloride and dried. After removal of the solvent the product distilled very uniformly at 84° at 65 mm. It was a colorless oil with the usual penetrating mercaptan odor; yield, 33%; d_{20}^{20} 1.13386; d_4^{20} 1.13186; n_D^{20} 1.5329; M_D (calcd.) 31.489; M_D (obs.) 31.302.

Anal. Subs., 0.2045: $BaSO_4$, 0.4203. Calcd. for C_5H_6OS: S, 28.09. Found: S, 28.23.

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[12] Steinkopf, Herold and Stöhr, *Ber.*, 53, 1007 (1920).

[13] Staudinger and Reichstein, Canadian Patent 283,765; C. A., 22, 4537 (1928).

α-**Furfuryl Ethyl Sulfide.**—The furfuryl mercaptan was converted into the previously unknown sulfide by treatment of its sodium derivative with ethyl bromide in alcoholic solution. Sodium bromide precipitated immediately and the reaction mixture was heated on a stearn-bath for one hour. On cooling the solution was decanted from the sodium bromide and after extraction of the sodium bromide with ether the solution and extract were distilled and the residue was fractionated in vacuum. The product, a colorless liquid of pungent odor, boiled at 90.5–91° at 28 mm.; yield, 80%; d_{20}^{20} 1.05144; d_4^{20} 1.04958; n_D^{20} 1.5140; M_D (calcd.) 41.005; M_D (obs.) 40.773.

Anal. Subs., 0.1983: $BaSO_4$, 0.3379. Calcd. for $C_7H_{10}OS$: S, 22.55. Found: S, 23.40.

Summary

1. By using a-furfuryl chloride as the starting material, the following new substances have been prepared: ethyl-a-furfurylmalonic ester, ethyl-a-furfurylbarbituric acid, a-furfurylacetoacetic ester, a-furfuryl nitrile, a-furylacetic acid, a-furfuryl thiocyanate and a-furfuryl ethyl sulfide.

2. The following substances, which had previously been prepared by indirect methods starting with furfural, have now been directly synthesized from a-furfuryl chloride: a-furfurylmalonic ester, a-furfurylbarbituric acid, 2-a-furfurylacetic acid, α-furfurylacetone and its semicarbazone and a-furfuryl mercaptan.

3. Ethyl-a-furfurylbarbituric acid has possibilities as an hypnotic. Its physiological activity is being studied and will be published later. It is expected that this study will yield some information concerning the effect of the a-furfuryl group upon physiological action.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OR THE UNIVERSITY OR NORTH CAROLINA]

PARA-CYMENE STUDIES. XIII. PARA-CYMYLHYDRAZINE-2 AND DERIVATIVES[1]

BY ALVIN S. WHEELER AND CHARLES L. THOMAS

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Phenylhydrazine is widely used in the identification of aldehydes and ketones. A limited number of its homologs have been prepared but phenylhydrazine remains the most available from the cost standpoint. The tolylhydrazines should follow and then cymylhydrazine. The latter compound seems to have been made so far in only one investigation.[2] It was not analyzed and a wide fraction, boiling at 110–120° at 1.5 mm., was taken as cymylhydrazine. The authors prepared the hydrochloride, the acetate and the hydrazones of glucose, mannose and galactose. The cymylhydra-

[1] This paper is an abstract of a thesis submitted by Charles L. Thomas in partial fulfilment of the requirements for the degree of Master of Science at the University of North Carolina in June, 1929.

[2] Kremers and Demonbreun, *J. Am.* Pharm. *Assocn.*, 12, 589 (1923).

zine was made by diazotizing 2-aminocymene with ethyl nitrite and reducing the diazo compound with stannous chloride. They found that when sodium nitrite was used a reddish brown tar was obtained. We used sodium nitrite, however, with very satisfactory results, but used sodium sulfite[3] instead of stannous chloride as reducing agent. Sometimes a tar was obtained but by boiling this with concd. hydrochloric acid it was partly converted into cymylhydrazine hydrochloride.

Not all condensation products of cymylhydrazine are stable. Kremers and Demonbreun could not isolate any product of the action of benzaldehyde or furfural. If obtained, it decomposed as soon as separated from the reaction mixture. The authors attributed these results to the steric hindrance of the *iso*propyl group. In our own work we failed to get a product with methyl ethyl ketone, acetophenone or benzaldehyde sufficiently pure for a good analysis. A peculiar reaction, as yet unexplained, was noted with carbon disulfide. Analysis gave exact figures for a ratio of two atoms of nitrogen for each atom of sulfur.

We prepared the hydrochloride, hydrobromide, sulfate and picrate of cymylhydrazine and condensations with benzophenone, salicylaldehyde and cinnamic aldehyde. The semicarbazide and thiosemicarbazide were readily made, also the *p*-nitrobenzoyl derivative. The product obtained from benzoyl chloride was amorphous and contained chlorine. No products were obtained by the action of methyl nonyl ketone, thionyl chloride, Michler's ketone and benzoylacetone.

Experimental

***p*-Cymylhydrazine-2,** $C_{10}H_{13}NHNH_2$.—Sixty cc. of 2-aminocymene (0.4 mole) was added with stirring to 88 cc. of concd. hydrochloric acid cooled by a freezing mixture; 100 g. of ice was then added and the stirring continued until a thick paste resulted. A solution of 33 g. of sodium nitrite in 75 cc. of water was added slowly, with ice also to keep the temperature around 0°. More sodium nitrite was added if complete solution did not take place. It is best to keep the temperature below 5° to prevent the formation of a green scum. The diazo solution was then poured rapidly with stirring into a freshly prepared solution of sodium sulfite, cooled to 5°. The sodium sulfite solution was prepared by dissolving 89 g. of sodium hydroxide in 600 cc. of water and passing in sulfur dioxide until the solution was slightly acid to phenolphthalein. After the diazo solution has been added to the sulfite solution it should be reddish-orange in color. The flask, which then contained 1 to 1.5 liters of solution, was heated on a hot-plate to 80–90° for one and one-half hours. The color darkened somewhat. Hydrochloric acid was then added until the odor of sulfur dioxide was distinctly noticeable. The heating was then continued for ten hours. The solution became a light yellow. After the period of ten hours a sample of about 10 cc. was removed and an equal volume of concd. hydrochloric acid added. If a reddish-brown tar separated, the heating was continued. If crystals were formed, the reaction was complete. The solution was cooled and 300 cc. of concd, hydrochloric acid added. The crystals obtained were dried

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[3] G. H. Coleman, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1922, Vol. II, p. 71.

and weighed; 58 g. or 72.5% of the theoretical yield. The crude product usually melts about 189°. It may be purified by boiling the aqueous solution with charcoal and reprecipitating with hydrochloric acid. Slow crystallization yields long white needles melting at 198°. This salt was prepared by Kremers and Demonbreun but they gave 186-187° as the melting point. On analysis we found for HCl, 17.95; calcd., 18.18. The free base was obtained by neutralizing the salt with sodium hydroxide, extracting with ether, drying and distilling at 5 mm. The fraction boiling from 129 to 132° was used for the determination of the constants. The drops of liquid at the top of the condenser appeared colorless but those falling into the receiver already had a slight yellow color. The liquid on standing in the dark slowly deepens in color. One preparation became cherry-red in the dark and sunlight brought the yellow color back. Cymylhydrazine is odorless and dissolves as completely in 50% acetic acid as phenylhydrazine. It melts at 26.5" and boils at 129–132" at 5 mm. Its density is d_{28}^{28} 0.9863; index of refraction at 25°, 1.5551. In the solid state it takes the form of long yellow needles.

Anal. Calcd. for $C_{10}H_{16}N_2$: N, 17.07. Found: N, 16.70.

Salts

Hydrobromide, $C_{10}H_{16}N_2 \cdot HBr$.—Long white needles, melting at 174°.

Anal. Calcd. for HBr: 33.05. Found: HBr, 33.00.

Sulfate, $C_{10}H_{16}N_2 \cdot H_2SO_4$.—Sulfuric acid of 1:1 strength was used. The last traces of acid were difficult to get rid of and the color was always slightly brown; small scales, melting at 130°.

Anal. Calcd. for H_2SO_4: 37.40. Found: H_2SO_4, 37.10.

Picrate, $C_{10}H_{16}N_2 \cdot C_6H_2OH(NO_2)_3$.—To a solution of 2 g. of the hydrochloride in 25 cc. of alcohol was added 2.3 g. of picric acid dissolved in the least possible amount of water. After several days the picrate separated out in long yellow needles. These decompose suddenly at 124°.

Anal. Calcd. for $C_{16}H_{19}O_7N_5$: N, 17.80. Found: N, 17.83.

Hydrazones

Cinnamylaldehyde-*p*-cymylhydrazone-2, $C_{10}H_{13}NHN{=}CHCH{=}CHC_6H_5$.—Equimolecular amounts of cinnamylaldehyde and cymylhydrazine were mixed. A noticeable rise in temperature took place and a yellow solid separated. The yield may be increased by heating for a short time on the water-bath. The product was recrystallized from dilute alcohol as thick picric yellow needles melting at 90°. The product is quite stable, for it turns brown only after standing about two months.

Anal. Calcd. for $C_{19}H_{22}N_2$: N, 10.08. Found: N, 9.88.

Salicylaldehyde-*p*-cymylhydrazone-2, $C_{10}H_{13}NHN{=}CHC_6H_4OH$.—Equal volumes of the components were mixed and heated for an hour on the water-bath. On cooling a mass of crystals separated. They crystallized from dilute alcohol in yellow needles melting at 87°. No signs of decomposition were visible after three months.

Anal. Calcd. for $C_{17}H_{20}ON_2$: N, 10.41. Found: N, 10.28.

Benzophenone-*p*-cymylhydrazone-2, $C_{10}H_{13}NHN{=}C(C_6H_5)_2$.—This compound could not be prepared by heating the components together. It was made by dissolving 2 g. of cymylhydrazine hydrochloride and 2 g. of benzophenone in 50 cc. of alcohol, adding a little sodium acetate and heating under a reflux for six hours. Upon cooling and adding water an oil separated. On standing for several days it turned red and red needles separated. The crystals came out of dilute alcohol in needles which were slightly brown, melting at 88°. No change in color occurred in two months.

Anal. Calcd. for $C_{23}H_{24}N_2$: N, 8.54. Found: N, 8.47.

Other **Hydrazones.**—A reaction was obtained with methyl ethyl ketone, the product consisting of plates, slightly brown, melting at 57°. It is unstable and the percentage found for nitrogen was 1.2 low. Acetophenone gave a product, consisting of mustard-yellow needles, melting at 84°. This was also unstable and the percentage for nitrogen was 1.2 low. The reaction with benzaldehyde gave an oil sometimes and again crystals which were light yellow leaflets. This product begins to decompose before it is dry. The crystals are exceedingly thin and give a fine display of interference colors.

Semicarbazides

p-Cymyl-1-semicarbazide-2, $C_{10}H_{13}NHNHCONH_2$.—Three g. of urea was added to 4 cc. of cymylhydrazine. Upon heating the urea melted and formed a layer underneath the hydrazine. Heating was continued until the two layers united. Upon cooling crystals separated. These were recrystallized from dilute alcohol, filtered and washed with water and ether, giving fine snow-white plates melting at 171°.

Anal. Calcd. for $C_{11}H_{17}ON_3$: N, 20.30. Found: N, 20.20.

p-Cymyl-1-thiosemicarbazide-2, $C_{10}H_{13}NHNHCSNH_2$.—An attempt to prepare this compound by heating the hydrazine with thiourea proved a failure. It was made by dissolving 3 cc. of cymylhydrazine in 10 cc. of glacial acetic acid and adding an excess of potassium thiocyanate. The mixture was warmed until complete solution took place. It was then cooled and poured into water. The solid product was recrystallized from dilute alcohol as flat white plates melting at 184". It turns slightly brown on standing.

Anal. Calcd. for $C_{11}H_{17}SN_3$: N, 18.84; S, 14.35. Found: N, 18.26; S, 14.28

Other Reactions

p-Nitrobenzoyl-p-cymylhydrazine-2, $C_{10}H_{13}NHNHCOC_6H_4NO_2$.—An attempt was made to prepare this compound by treating a mixture of cyrnylhydrazine hydrochloride and p-nitrobenzoyl chloride with sodium hydroxide, but no product could be isolated. It was then found that cymylhydrazine and nitrobenzoyl chloride unite in benzene solution without the evolution of hydrochloric acid gas to give a light yellow crystalline compound. It contained hydrochloric acid and melted at 160°. If sodium hydroxide and dilute alcohol are added to the product, the liquid becomes deep purplish-brown. If the mixture is heated until all of the solid goes into solution and then is neutralized with acid, a precipitate is thrown down. This was recrystallized from dilute alcohol, forming long yellow needles melting at 177".

Anal. Calcd. for $C_{13}H_{19}O_3N_3$: N, 13.41. Found: N, 13.16.

Reaction with Carbon **Disulfide.**—Two volumes of the hydrazine were mixed with five volumes of carbon disulfide and heated on the water-bath for an hour. Hydrogen sulfide was evolved and a deep yellow to green precipitate formed. Upon cooling the substance turned to a transparent resin. This was covered with much petroleum ether and worked with a glass rod. The resin turned to a mass of small white crystals which melted at 177°.

Anal. Found: *N*, 18.75; S, 21.25. These results indicate two atoms of nitrogen for one of sulfur.

Summary

1. p-Cymylhydrazine-2 was prepared by diazotizing 2-arninocyrnene and reducing the product with sodium sulfite. The hydrochloride, hydrobromide, sulfate and picrate were made.

2. Cymylhydrazones of cinnamylaldehyde, salicylaldehyde and benzophenone were made. The hydrazones of methyl ethyl ketone, acetophenone and benzaldehyde were found to be unstable.
3. p-Cymyl-1-semicarbazide-2 and *p*-cymyl-1-thiosemicarbazide-2 were prepared.
4. A p-nitrobenzoyl derivative was prepared.
5. Cymylhydrazine reacts with carbon disulfide to give a product whose nature was not solved.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY, FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE, IN COOPERATION WITH THE UNIVERSITY OF WISCONSIN]

SEQUOYITE, A CYCLOSE FROM REDWOOD (SEQUOIA SEMPERVIRENS)

BY E. C. SHERRARD[1] AND E. F. KURTH[2]

RECEIVED JUNE 10, 1929 PUBLISHED OCTOBER 5, 1929

In a recent paper[3] we reported the isolation of a new cyclose which occurs with pinite in the cold-water extract of the heartwood of redwood. First analyses indicated that the new compound might have the empirical formula $C_8H_{16}O_7$, but later analyses upon purer and larger amounts of the material proved that it is a monomethyl ether of *i*-inosite and is isomeric with pinite, bornesite and quebrachite. The present paper describes the details of isolation, the experimental results that convinced us of its structural formula and the preparation of some of its derivatives.

Sequoyite, as we have named it, was isolated from the aqueous extract of redwood in a manner similar to that employed for pinite. The two cycloses crystallized out together upon the addition of alcohol to the thick, concentrated extract. They were separated from each other by fractional crystallization; sequoyite, being less soluble in either alcohol or water, crystallized readily from a 50% alcoholic solution, while the pinite crystallized slowly from a 70% solution.

The impure sequoyite crystals were purified by warming with a small amount of barium hydroxide, then filtering off the precipitated gums and coloring matter and acidifying the filtrate with sulfuric acid to remove the excess barium. The solution that remained after filtering off the barium sulfate was nearly colorless. The new cyclose was obtained from this solution by concentrating it to a thin sirup and then diluting it with

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[3] Sherrard and Kurth, *Ind. Eng. Chem.*, **20**, 722 (1928).

alcohol. The crystals were finally obtained in the pure state after recrystallization from alcohol and water.

The yield on the basis of the weight of the oven-dried heartwood varied from traces to 0.06%.

When pure, sequoyite crystallizes from alcohol and water in small transparent prisms which melt at 234–235° (uncorr.) and sublime at temperatures above this. It has a sweet taste, is readily soluble in water, is only slightly soluble in hot alcohol and is insoluble in ether, benzene or carbon tetrachloride. It is optically inactive, does not reduce Fehling's reagent, gives no precipitate with phenylhydrazine and is not affected by dilute acids or alkalies. When heated with nitric acid it is oxidized to oxalic acid. In cold, concentrated sulfuric acid it dissolves slowly without charring. It is not affected by acetic anhydride at room temperature.

Anal. Calcd. for $C_7H_{14}O_6$: C, **43.27; H, 7.27.** Found: C, **43.11, 43.31, 43.20;** H, **7.24, 7.30, 7.28.** Calcd. for $C_6H_{11}O_5OCH_3$: OCH_3, **15.9.** Found: OCH_3, **14.87, 15.3, 16.4.** Determination of the molecular weight by cryoscopic methods gave **188** and **197.**

Sequoyite Pentacetate.—The new cyclose was acetylated by boiling 1 g. of the pure crystals with an equal weight of anhydrous sodium acetate and **15** cc. of acetic anhydride for one hour in an oil-bath. Upon adding water to the cooled reaction mixture, the pentacetate separated out. It was recrystallized from hot alcohol.

Sequoyite pentacetate is obtained from hot alcohol in small, needle-like crystals which melt at 198° (uncorr.) and sublime at temperatures above this. It is also soluble in ether and is insoluble in water.

Anal. Calcd. for $C_6H_6(O_2C_2H_3)_5OCH_3$: **C, 50.47;** H, **5.98;** CH_3CO, **53.22.** Found: **C, 50.26, 50.50; H, 5.86, 5.82;** CH_3CO, **52.62, 52.78,** 52.60.

The percentage of acetyl was determined by hydrolyzing the pentacetate with sodium hydroxide and also with barium hydroxide.

In hydrolyzing with sodium hydroxide, the acetylated compound was boiled for one-half hour with an excess of the $N/10$ alkali. It was then rapidly cooled, phenolphthalein was added and the amount of alkali required for hydrolysis was determined by titrating with standard acid.

In the barium hydroxide method the acetylated compound was boiled for two and a half hours in a reflux apparatus using a **1:1** solution of methyl alcohol and water as a solvent. The product was filtered, the filtrate was treated with carbonic anhydride in excess, was again filtered and the final filtrate was then evaporated. The residue was dissolved in water, the liquid was Ntered and the barium in the filtrate was determined as sulfate. The original sequoyite was recovered by this method and retained a melting point of **235".**

From the hydriodic acid residue remaining from the methoxyl determinations, inactive inosite was obtained. It is formed when sequoyite is heated with hydriodic acid, reacting in accordance with the following equation:

$$C_6H_6(OH)_5OCH_3 + HI = C_6H_6(OH)_6 + CH_3I$$

It was separated from the reaction mixture by evaporating off the hydriodic acid in a steam-bath, dissolving the residue in a small amount of warm water and precipitating with alcohol. When recrystallized from alcohol and water it melted at 224° (corr.). The hexacetate derivative was prepared and it melted at 215° (corr.).

When 1.0688 g. of sequoyite was heated with hydriodic acid in a small distilling flask, 0.9192 g. or 86.0% of the sequoyite was recovered as i-inosite and a sufficient amount of the methyl iodide was collected for a boiling-point determination. It boiled between 43 and 44°. A maximum yield of 93.1% of the theoretical amount of i-inosite or 89.4% of the weight of the sequoyite was obtained from a hydriodic acid residue remaining from a methoxyl determination.

A careful investigation of the chemical literature indicates that no compound with the properties here described has been previously reported. We are therefore convinced that we have isolated a new cyclose. Since methyl iodide and *i*-inosite are the only decomposition products obtained and since they are obtained in the proportion corresponding to a compound having the molecular formula $C_6H_6(OH)_5OCH_3$, sequoyite must be a monomethyl ether of inactive inosite.

Summary

1. The isolation of a new cyclose from the heartwood of redwood has been described.

2. Experimental results show that this compound is a monomethyl ether of i-inosite.

3. Upon heating with hydriodic acid, two decomposition products are obtained and have been identified as methyl iodide and i-inosite.

4. The pentacetate derivative has been prepared and described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

1,2-BENZ-3,4-ANTHRAQUINONE

BY LOUIS F. FIESER AND EMMA M. DIETZ

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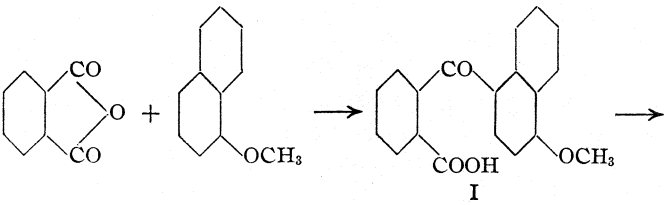
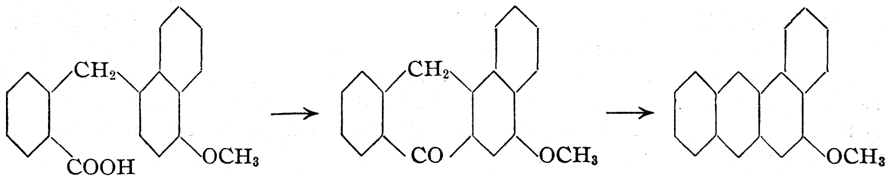
In connection with a study of the reduction potentials of some of the higher benzologues of anthraquinone and phenanthrenequinone, we became interested in securing the compound named in the title. A suitable method of preparing the quinone was found in the oxidation of 4-amino-3-hydroxy-1,2-benzanthracene, which, in turn, was obtained from 3-hydroxy-1,2-benzanthracene.

The synthesis of the methyl ether of 3-hydroxy-1,2-benzanthracene, IV, was accomplished in the following manner

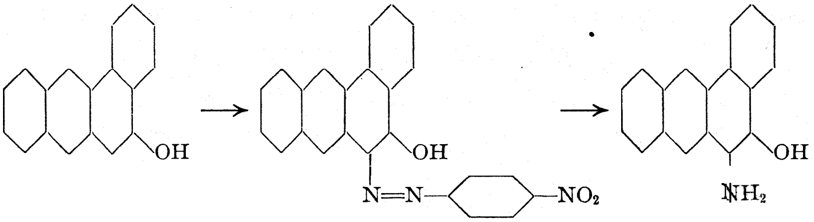




II III IV

2-(4'-Methoxy-naphthoyl-1')-benzoic acid, I, has been described by Scholl, Seer and Zincke,[1] and the structure which they assumed for the acid is established by the present work. By using tetrachloro-ethane rather than nitrobenzene as the solvent in carrying out the Friedel and Crafts reaction, their method of preparation became easily applicable to quantity production. While the keto-acid, I, failed to condense easily to give an anthraquinone, the condensation of the reduction product, II, to the anthrone, III, was accomplished readily by dissolution in cold, concentrated sulfuric acid. 3-Methoxy-1,2-benz-10-anthrone, III, is a rather unstable compound and it was isolated only in the form of the acetyl derivative of the enol modification. It was reduced to 3-methoxy-1,2-benzanthracene, IV, with aluminum amalgam and ammonia in alcoholic suspension, according to the general method of Hall and Perkin.[2] Owing to side reactions, the yield was only about 55%.

On hydrolysis of the ether with a hydrobromic acid–glacial acetic acid mixture, 3-hydroxy-1,2-benzanthracene (V) was obtained. This phenol, which was characterized by the preparation of a number of derivatives, is only very sparingly soluble in alkali and it failed to couple with diazotized sulfanilic acid under a variety of conditions. An azo compound was obtained only by the use of the method which Meyer, Irschick and Schlosser developed for carrying out the coupling reaction with phenol ethers.[3] By the interaction of 3-hydroxy-1,2-benzanthracene and *p*-nitrobenzene diazonium sulfate in glacial acetic acid solution the dyestuff, VI, was produced without difficulty. Being only very sparingly soluble in organic solvents or in alkali, the dyestuff is not easily reduced by the usual methods, but a satisfactory means of preparing the amine, VII, was found in the re-



V VI VII

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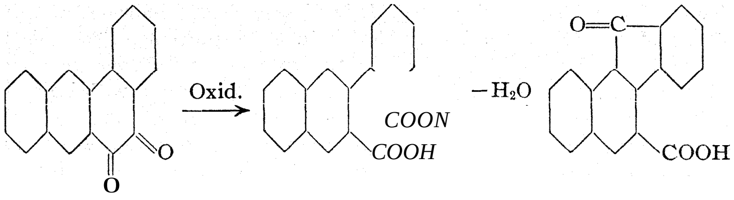
[1] Scholl, Seer and Zincke, *Monatsh.*, 41, 598 (1920).

[2] Hall and Perkin, *J. Chem. Soc.*, 123, 2029 (1923).

[3] Meyer, Irschick and Schlosser, *Ber.*, 47, 1747 (1914).

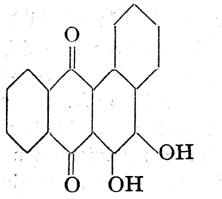
duction of the azo compound with stannous chloride in a boiling butyl alcoholic suspension.

The hydrochloride of 4-amino-3-hydroxy-1,2-benzanthracene yielded 1,2-benz-3,4-anthraquinone, VIII, on oxidation in glacial acetic acid solution. The quinone crystallizes in bright red needles and forms a bisulfite addition product. It was converted by oxidation with hydrogen peroxide in glacial acetic acid solution into a substance having the properties of a diphenic acid derivative. This acid, to which the structure of 4,5-benzodiphenyl-2,2′-dicarboxylic acid, IX, may be assigned, was condensed by the action of concentrated sulfuric acid to a yellow fluorenone-carboxylic acid which probably has the structure of X, though the structure of 2,3-benzofluorenone-5-carboxylic acid is also possible. These facts indicate that the quinone in question is of the ortho type and similar to 9,10-phenanthrenequinone, hence that it has the structure of VIII.

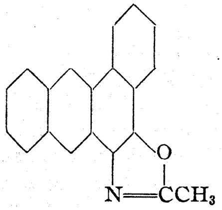


VIII IX X

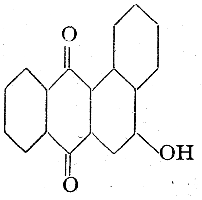
The structure of the hydroxybenzanthracene, V, is fixed by the method of synthesis and the structure of the above ortho-quinone; but the following independent evidence also may be cited. By the reductive acetylation of 1,2-benz-3,4-anthraquinone, followed by oxidation and by hydrolysis of the oxidation product, there was obtained the dihydroxy-1,2-benz-9,10-anthraquinone, XI. The compound gives an intense coloration with Dimroth's boro-acetic anhydride reagent,[4] showing that one hydroxyl group is adjacent to a quinonoid carbonyl group. The second hydroxyl group must be ortho to the first, for the hydroxybenzanthracene couples in the ortho position, as shown by the formation of an oxazole derivative, XII, from 4-amino-3-hydroxy-1,2-benzanthracene. The dihydroxyquinone, XI, could be formed from either 3- or 4-hydroxy-1,2-benzanthracene, but the latter possibility is excluded by the fact that the monohydroxy-1,2-



XI



XII



XIII

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[4] Dimroth and Faust, *Ber.*, **54**, 3020 (1921); Dimroth, *Ann.*, **446**, 97 (1926).

benz-9,10-anthraquinone (XIII), prepared by the oxidation of the acetyl derivative and the hydrolysis of the oxidation product, gives a negative result in the Dimroth test.

Experimental Part

2-(4'-Methoxynaphthoyl-1')-benzoic Acid (I).—To a solution of 78 g. of α-methoxynaphthalene and 78 g. of phthalic anhydride in 400 cc. of tetrachloro-ethane there was added 150 g. of powdered aluminum chloride in three portions. The mixture was stirred mechanically at room temperature for twelve hours and allowed to stand for an equal period of time. The dark addition product was decomposed with ice and hydrochloric acid and the solvent was removed by steam distillation. This operation was completed in a small fraction of the time required when nitrobenzene was employed as the solvent. The granular, brown residue was dissolved in the requisite quantity of hot sodium carbonate solution, the solution was treated with animal charcoal and then 50 cc. of 6 *N* sodium hydroxide solution was added. The sodium salt of the acid separated from the cooled solution in the form of colorless crystals. When washed with sodium chloride solution and dried, the product contained a small quantity of sodium chloride but it was otherwise pure and the salt was well suited for carrying out the following reaction; yield, 147 g. (91%). The acid obtained from this sodium salt melted at 196–197° (Scholl, Seer and Zincke, 193–194°).

(4-Methoxynaphthyl-1)-phenylmethane-2′-carboxylic Acid (II).—A solution of 86 g. of the sodium salt of 2-(4'-methoxynaphthoyl-1')-benzoic acid and 104 g. of sodium hydroxide in 1.5 liters of water was treated with 145 g. of zinc dust and the mixture was heated so as to maintain a lively evolution of gas for ten hours. The hot solution was filtered, the zinc was extracted with several portions of boiling water and 50 cc. of 6 N sodium hydroxide was added to the filtrate. The sodium salt often separated in an oily condition but it soon crystallized. The material was washed with sodium chloride solution, dissolved in water and converted into the free acid. Prepared by precipitation, the acid was not easily collected by filtration until it had been coagulated somewhat by heating the mixture to the boiling point. A colorless product melting at 215–219° and requiring no further purification was obtained; yield, 75 g. (91%).

The acid dissolves readily in alcohol, benzene or glacial acetic acid. It forms colorless plates melting at 217–219° (221–223°, corr.).

Anal.[5] Calcd. for $C_{19}H_{16}O_3$: C, 78.07; H, 5.52. Found: C, 78.01; H, 5.62.

3-Methoxy-1,2-benz-10-anthrone (III).—The above acid dissolves in cold, concentrated sulfuric acid to give a deep red solution and ring closure takes place without side reactions. Twenty grams of the powdered acid was stirred into 220 cc. of concentrated sulfuric acid at 20° and after forty-five minutes the solution was slowly poured into 1.2 liters of a well-stirred mixture of ice and water. This precipitated a finely divided, pale yellow product which was collected and washed with dilute ammonia solution. The anthrone is very sensitive to heat and to oxygen, particularly when in solution, and it was not purified for analysis. A glacial acetic acid solutioa rapidly turned dark green and deposited a brown, amorphous material while still well below the boiling point. The anthrone dissolves readily in alcohol or benzene, but the solutions darken rapidly; it dissolves slowly in alkali.

For purposes of identification the acetyl derivative of the anthranol form was prepared by boiling for a short time a solution of 0.7 g. of the anthrone in 3 cc. of pyridine and 5 cc. of acetic anhydride. The product, crystallized from benzene–ligroin and from alcohol, formed colorless needles melting at 194° (197' corr.).

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[5] The Dennstedt platinum contact star was employed in carrying out all of the analyses reported.

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.72, H, 5.10. Found: C, 79.76; H, 5.14.

3-Methoxy-1,2-benzanthracene (IV).—The reduction of the anthrone was carried out in alcoholic suspension with aluminum amalgam and ammonia, a method employed extensively by Hall and Perkin.[2] In the present case the reaction is difficult to control and the formation of by-products greatly decreases the yield. It was found advisable to work with no more than 20 g. of material at one time and to prepare the amalgam very carefully, according to the directions of Wislicenus.[6] Twenty grams of aluminum turnings was etched with 10% sodium hydroxide, washed with water, shaken for one-half minute with a 0.5% mercuric chloride solution, washed again, and the whole process was repeated, The resulting amalgam was added to 960 cc. of alcohol and the mixture was heated to obtain a lively gas evolution. The cake of moist anthrone obtained as above from 20 g. of (4-methoxynaphthyl-1)-phenylmethane-2′-carboxylic acid was broken into large pieces and introduced into the mixture. Sixty cc. of concentrated ammonia solution was then added gradually. The mixture was boiled under the reflux condenser for four hours, 30 cc. of ammonia solution and the amalgam from 10 g. of aluminum being added after the second and third hours. The light yellow solution rapidly became deep red and later pale yellow or pink, while much aluminum hydroxide separated. At the end of the reaction the liquid was decanted, treated with 250 cc. of concentrated hydrochloric acid and heated to the boiling point in order to dissolve the hydroxide, which otherwise occludes much material. An equal volume of water was added, the solution was cooled and the material which separated was collected and again digested with hydrochloric acid. The dried residue (17 g.) contained some inorganic material. It was extracted twice with benzene and the well-concentrated, dark red solution deposited 10 g. of straw-colored needles, m. p. 165–167°.

3-Methoxy-1,2-benzanthracene is very soluble in benzene or chloroform, moderately soluble in alcohol or glacial acetic acid, and the solution in the latter solvent has a violet fluorescence. The pure material forms colorless needles melting at 167–168°.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.47. Found: C, 88.03; H, 5.47.

When the preparation was carried out exactly as described above, the yield was usually from 45 to 55% of the theoretical, though in two instances it rose to 65%. The results were much poorer (25%) when the mixture was stirred and when the anthrone was added in very small portions. In this instance it was possible to isolate a considerable quantity of a yellow by-product which melted at 272° and which was less soluble than 3-methoxy-1,2-benzanthracene. The yellow substance contains a higher percentage of oxygen than the original material and it is probably a dimolecular product. Traces of the substance were always present in the residue after extracting the main product with benzene.

3-Methoxy-1,2-benz-9,10-anthraquinone.—3-Methoxy-1,2-benzanthracene was oxidized in glacial acetic acid solution at 90° with chromic acid. The oxidation product, precipitated by the addition of water after one-half hour, was crystallized from methyl ethyl ketone and from benzene. It forms brown-red needles melting at 188.5°. It forms a red vat with alkaline hyposulfite solution, while the solution in concentrated sulfuric acid is intensely blue-green. The quinone is moderately soluble in benzene or glacial acetic acid and only slightly soluble in alcohol.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.13; H, 4.20. Found: C, 78.96; H, 4.19.

3-Hydroxy-1,2-benzanthracene (V).—The hydrolysis of 3-methoxy-1,2-benzanthracene was accomplished by the use of hydrobromic acid. Aluminum chloride had no effect in carbon disulfide solution and when heated with the solid material it caused decomposition. A hot, stirred solution of 33 g. of the ether in 1 liter of glacial acetic

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[6] Wislicenus, *J. prakt. Chem.*, [2] **54**, 54 (1896).

acid was treated with 43 cc. of 40% hydrobromic acid and boiled for one and three-quarters hours. The color changed from yellow to dark green to red-brown and finally to a pale orange. On adding 50 cc. of water to the solution and cooling, 27.2 g. (87.5%) of nearly pure, greenish-yellow needles separated. Recrystallization from toluene removed a trace of green material and small, orange-yellow needles were obtained. The substance melts with decomposition at about 196–205° and imparts an orange color to the glass capillary. It is moderately soluble in toluene, less soluble in alcohol, and the sodium salt, which is yellow, is very sparingly soluble. The solutions darken on long heating, The material may be distilled at a reduced pressure without much decomposition if care is taken to avoid contact of the hot material with the air.

Anal. Calcd. for $C_{18}H_{12}O$: C, 88.50; H, 4.96. Found: C, 88.47; H, 4.81.

3-Acetoxy-1,2-benzanthracene.—Prepared by boiling a solution of the hydroxy compound in acetic anhydride for one hour, and crystallized from benzene and from benzene–ligroin, the acetate formed colorless needles melting at 129°.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83 93; H, 4.93. Found: C, 83 67; H, 4.99.

3-Acetoxy-1,2-benz-9,10-anthraquinone.—The oxidation of the acetate with chromic acid in glacial acetic acid proceeded smoothly and in nearly quantitative yield when the solution was kept at a temperature of 70°. The quinone, which is moderately soluble in toluene or glacial acetic acid, formed small, yellow crystals melting at 232°.

Anal. Calcd. for $C_{20}H_{12}O_4$: C, 75.93; H, 3.83. Found: C, 76.13; H, 4.00.

3-Hydroxy-1,2-benz-9,10-anthraquinone (XIII) was prepared, but not purified for analysis, by warming the acetate with alcoholic alkali. The intensely purple solution which resulted deposited a light brown product on acidification. The quinone dissolves in concentrated sulfuric acid with an intense blue-green color; in pyridine it forms a dark orange-red solution; while the solution in boro-acetic anhydride is pale yellow. The alkali salts of the quinone dissolve with difficulty in water but give purple solutions in alcohol; the vat is orange.

4-Amino-3-hydroxy-1,2-benzanthracene (VII).—This compound was prepared in the form of the hydrochloride and analyzed as the triacetate. It was obtained from 3-hydroxy-1,2-benzanthracene by the formation and reduction of an azo dye. Attempts to couple this phenol with diazotized sulfanilic acid in aqueous or alcoholic suspension or in pyridine solution were unsuccessful, but it was found possible to prepare **4-(*p*-Nitrobenzene-azo)-3-hydroxy-1,2-benzanthracene (VI)** in the following manner. Sixteen and seven-tenths g. of p-nitro-aniline was converted into p-nitrobenzene diazonium sulfate as described by Meyer, Irschick and Schlosser[3] and dissolved in glacial acetic acid. On adding this solution to a well-stirred, cooled solution of 15 g. of 3-hydroxy-1,2-benzanthracene in 1250 cc. of glacial acetic acid, a dark red dyestuff separated immediately. On completion of the reaction the solution was diluted with water and the product was collected. The substance is insoluble in alkali and sparingly soluble in most organic solvents, It dissolves fairly readily in nitrobenzene but does not form good crystals suitable for analysis.

For the reduction of the dye it is advisable to use the moist material. The above product was suspended in 850 cc. of n-butyl alcohol containing 100 g. of stannous chloride and 200 cc. of concentrated hydrochloric acid. The mixture was stirred mechanically and heated at the boiling point for four to five hours, when all of the dye had dissolved to give a clear orange solution. On adding 150 cc. of concentrated hydrochloric acid and cooling, pale yellow crystals of the amine hydrochloride separated. A further quantity (3 g.) was obtained on concentrating the mother liquor in a vacuum; yield, 21 g. Dried at room temperature, the material contained some solvent, but only traces of tin. In solution the substance decomposes very easily in the absence of a reducing agent and an analytically pure sample was not obtained. It is sparingly soluble in water but soluble in alcohol. For purposes of characterization it was converted into the following derivatives.

Triacetate of 4-amino-3-hydroxy-1,2-benzanthracene.—This was prepared by boiling for one hour an acetic anhydride solution of equal parts of the amine hydrochloride and fused sodium acetate. The product was not homogeneous but the less soluble fraction yielded, after repeated crystallization, a substance crystallizing in colorless plates and melting constantly at 199-201° (203–205°, corr.). The compound is insoluble in acids or alkalies and dissolves readily in benzene or glacial acetic acid. It is converted by distillation into the oxazole derivative.

Anal. Calcd. for $C_{24}H_{19}O_4N$: C, 74.78; H, 4.97. Found: C, 74.27, 74.13; H, 5.13, 5.22.

Oxazole Derivative of 4-amino-3-hydroxy-1,2-benzanthracene (XII).—The crude product obtained on acetylating in the manner described above was distilled *in vacuo*. After the removal of acetic acid and anhydride, the oxazole distilled as a yellow oil which soon solidified. It is only moderately soluble in glacial acetic acid but it dissolves easily in benzene and separates in dusters of light yellow needles, m. p. 175.5".

Anal. Calcd. for $C_{20}H_{13}ON$: C, 84.78; H, 4.63. Found: C, 84.99, 85.05; H, 5.05, 5.00.

1,2-Benz-3,4-anthraquinone (VIII).—The 4-amino-3-hydroxy-1,2-benzanthracene obtained from 15 g. of 3-hydroxy-1,2-benzanthracene was largely dissolved in 670 cc. of glacial acetic acid, a solution of 5 g. of chromic anhydride was added at 100° and the temperature was held there for fifteen minutes. On adding water a dull red product was obtained. The quinone was extracted with toluene from some dark brown material, giving 8.1 g. of bright red needles. The yield from 3-hydroxy-1,2-benzanthracene was 57% of the theoretical.

The quinone is moderately soluble in toluene or glacial acetic acid, less soluble in benzene or alcohol. The solution in concentrated sulfuric acid is purple in color; in pyridine it is red-orange, The quinone dissolves slightly in hot concentrated bisulfite solution and precipitates on the addition of sodium carbonate. The pure material forms red needles melting with some decomposition at 254-255" (262–263°, corr.).

Anal. Calcd. for $C_{18}H_{10}O_2$: C, 83.70; H, 3.90. Found: C, 83.56; H, 3.79.

3,4-Diacetoxy-1,2-benzanthracene.—The quinone was reduced and acetylated by heating a mixture with equal parts of zinc dust and fused sodium acetate and with 10 parts of acetic anhydride for one-half minute, when the original dark green color was replaced by a clear orange. An equal volume of glacial acetic acid was added and the heating continued pntil all of the quinone had dissolved and the solution had lost all red color, but the heating was discontinued at the first sign of darkening. A pale yellow product was obtained on decanting into water. The substance dissolves readily in benzene and forms plates containing solvent of crystallization. From methyl alcohol, in which it is much less soluble, small, faintly pink needles were obtained. The solution in benzene has a marked blue fluorescence. The melting point is 197° (201°, corr.).

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.72; H, 4.69. Found: C, 76.47; H, 4.69.

3,4-Diacetoxy-1,2-benz-9,10-anthraquinone.—The oxidation of the above diacetate was carried out with an equal weight of chromic anhydride in glacial acetic acid solution at 70°, the yield being nearly quantitative. The quinone crystallizes from benzene or glacial acetic acid in the form of small, yellow prisms melting at 198-199°.

Anal. Calcd. for $C_{22}H_{14}O_6$: C, 70.58; H, 3.77. Found: C, 70.75; H, 3.83.

On hydrolysis of the quinone with alcoholic alkali, **3,4-dihydroxy-1,2-benz-**

9,10-anthraquinone (XI) was obtained as a purplish black powder. The solutions of the quinone in organic solvents are red or purple. The color in concentrated sulfuric acid is an intense Prussian blue and in warm pyridine it is orange red. The alkaline solution is bluish green; the solution in acetic anhydride is pale red and in boro-acetic anhydride it is an intense chrome green. The structure of this dihydroxyquinone is a combination of those of alizarin and of 1,2-benzanthraquinone, both of which are valuable dyes; but the compound is too sparingly soluble in water to be applied to mordanted cloth and the greenish blue dyeing imparted to cotton on vatting is not fast to washing with soap.

4,5-Benzodiphenyl-2,2'-dicarboxylic Acid (IX).—This acid resulted from the oxidation of 1,2-benz-3,4-anthraquinone. A solution of 3 g. of the quinone in 300 cc. of glacial acetic acid was treated with 2 cc. of 30% hydrogen peroxide and the temperature was maintained at 90° for one hour, when the original red color had paled somewhat. After a second addition of peroxide, the solution was allowed to stand for ten hours and then it was concentrated to a small volume and diluted with water. A light brown oil separated and soon crystallized. After precipitation from a sodium carbonate solution, the material was crystallized from dilute methyl alcohol, when it formed slightly tan microcrystals melting at 246° (252°, corr.). The yield was 2.6 g.

Anal. Calcd. for $C_{18}H_{12}O_4$: C, 73.96; H, 4.14. Found: C, 74.08; H, 4.18.

1,2-Benzofluorenone-4-carboxylic Acid (X) (or 2,3-Benzofluorenone-5-carboxylic Acid).—A solution of 0.6 g. of 4,5-benzodiphenyl-2,2'-dicarboxylic acid in 50 cc. of concentrated sulfuric acid was allowed to stand for several hours; the dark green solution was then poured into water and the fine yellow precipitate was collected. The product appeared to be homogeneous. It dissolved readily in glacial acetic acid and the solutions tended to remain supersaturated. It crystallizes well from toluene, in which it is moderately soluble, forming slender, yellow needles melting at 261° (268°, corr.).

Anal. Calcd. for $C_{18}H_{10}O_3$: C, 78.83; H, 3.68. Found: C, 78.79; H, 3.90.

Summary

3-Methoxy-1,2-benzanthracene has been synthesized from phthalic anhydride and α-methoxynaphthalene and converted into 3-hydroxy-1,2-benzanthracene. The latter compound was converted, through the p-nitrobenzene-azo derivative, into the 4-amino derivative, which yielded 1,2-benz-3,4-anthraquinone on oxidation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE CONSTITUTION AND THE DISSOCIATION OF THE GRIGNARD REAGENT[1]

BY HENRY GILMAN AND ROBERT E. FOTHERGILL

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Introduction

It is possible to write a large number of formulas for the Grignard reagent prepared in ether. The so-called central element to which might be attached the largest number of other elements and groups can be magnesium (variously coordinated) or oxygen or a halogen. Or we might have combinations of two or more of such central atoms, and structures involving residual valences of carbon and even of hydrogen. Then there are electronic interpretations of the structure, which because of the polar characteristics of organomagnesium halides may have formal, classical bonds replaced by electrostatic forces after some representations of the structure of compounds like magnesium chloride.

If we omit the diethyl ether, which is not a ***necessary***[2] part of the molecule, it is possible to simplify matters considerably by restricting discussion arbitrarily to two formulas to which most attention has been directed recently.[3] These formulas are

$$\text{(A) } 2RMgX \text{ and } R_2Mg{\cdot}MgX_2 \text{ (B)}$$

One of several ways of deciding between these two formulas is to determine whether MgX_2 is an integral part of the Grignard reagent. Some light can be thrown on this by use of the very interesting recent studies of Gomberg and Bachmann[4] on the following equilibrium

$$MgI_2 + Mg \rightleftarrows 2MgI \qquad \text{(I)}$$

The magnesious halide formed in accordance with Reaction I can be characterized in a number of ways, particularly by its reaction with benzophenone to give benzopinacol

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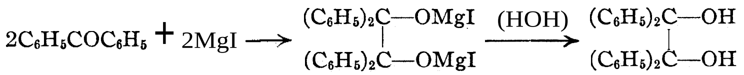
[1] An account of this work was read at the Spring Meeting of the American Chemical Society held at Columbus, Ohio, in April, 1929.

[2] It is possible to prepare RMgX compounds with no ether, and it is possible to remove all ether from RMgX compounds. These so-called "individual organomagnesium halides" show the general reactions of the corresponding compounds containing ether.

[3] It is out of the question, because of space limitations, to give a complete (even though uncritical) consideration of the large amount of work on the constitution of organomagnesium halides. Some leading references are Grignard, *Compt. rend.*, 130, 1322 (1900); 185, 507 (1927); Bull. *soc. chim.*, 41, 759 (1927); Jolibois, *Comfit. rend.*, 155, 353 (1912); Meisenheimer and co-workers, *Ber.*, 54, 1655 (1921); 61, 708, 720 (1928); Ivanoff, *Compt. rend.*, 185, 505 (1927); Terentieff, *Z. anorg. Chem.*, 156, 73 (1926); Kierzek, Bull. *soc. chim.*, 41, 1299 (1927); Schlenk and Schlenk, *Ber.*, 62, 923 (1929). A list of general references may be found in Footnote 3 on p. 748 of an article by Gilman, Fothergill and Parker, *Rec. trav. chim.*, 48, 748 (1929).

[4] Gomberg and Bachmann, THIS JOURNAL, 49, 236, 2584 (1927).



$$2C_6H_5COC_6H_5 + 2MgI \longrightarrow \begin{array}{l}(C_6H_5)_2C\text{—}OMgI \\ \quad | \\ (C_6H_5)_2C\text{—}OMgI\end{array} \xrightarrow{(HOH)} \begin{array}{l}(C_6H_5)_2C\text{—}OH \\ \quad | \\ (C_6H_5)_2C\text{—}OH\end{array} \qquad \text{(II)}$$

If the Grignard reagent has Formula B and if, also, the MgX_2 part of the molecule has an attachment to the rest of the molecule of a kind that will permit its reaction with magnesium to give magnesious halide (Reaction I), then on the addition to the Grignard reagent of one equivalent of magnesium and two equivalents of benzophenone, benzopinacol should result in equivalent quantities, together with a tertiary alcohol formed as follows

$$R_2Mg \text{ (or } RMgX) + (C_6H_5)_2CO \longrightarrow R(C_6H_5)_2COH \qquad \text{(III)}$$

The results reported at this time of several experiments made with typical organomagnesium halides show that the Grignard reagents are better represented by the RMgX formula. We do not mean by this that no benzopinacol was formed. Actually some benzopinacol was obtained in many of the reactions. This, of course, might have been predicted because the reaction between an RX compound and magnesium is not simple[5] and invariably leads to the formation of small (and in some cases large) quantities of MgX_2.[6] Obviously the presence of such MgX_2 compounds, formed incidentally to side reactions, would make it possible for benzopinacol to be formed in accordance with Reactions I and II. The quantity of benzopinacol formed in this way is apparently proportional to the quantity of MgX_2 formed. This was strikingly illustrated in two experiments carried out with *n*-butylmagnesium iodide. In one case the butyl iodide was added rapidly to the magnesium in ether, and in the other experiment it was added slowly. In the former case the yield of Grignard reagent is lower[6] because of the larger formation of magnesium iodide, and in agreement with this a greater quantity of benzopinacol was obtained in the experiment carried out with a more rapid addition of the butyl iodide.

Furthermore, no benzopinacol was obtained in the reactions involving organomagnesium *chlorides*.[7] This is in strict agreement with the experiments of Gomberg and Bachmann,[4] in which it was shown that magnesium chloride, very probably because of its sparing solubility, does not react with magnesium after Reaction I to give magnesious chloride (—MgCl).

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[5] Gilman and Fothergill, THIS JOURNAL, 50, 3334 (1928). This paper discusses some side reactions in the preparation of alkylmagnesium halides. Related work is by Gilman and Kirby, *ibid.*, 51, 1571 (1929).

[6] Very recent work on the yields of some Grignard reagents, with leading references to earlier work, is to be found in papers by Gilman, Zoellner and Dickey, *ibid.*, 51, 1576, 1583 (1929).

[7] With the exception of the special cases of *tert.*-butylmagnesium and triphenylmethylmagnesium chlorides; see the latter part of the Introduction and also the Experimental Part.

From such evidence it appears that there is little or no $R_2Mg{\cdot}MgX_2$ in the Grignard reagent. This found some support in a reaction carried out between magnesium diethyl, magnesium iodide, magnesium and benzophenone in which no benzopinacol was obtained. One interpretation of this reaction is that the magnesium diethyl and magnesium iodide reacted as follows

$$(C_2H_5)_2Mg + MgI_2 \longrightarrow 2C_2H_5MgI \qquad \text{(IV)}$$

In other words, an R_2Mg compound cannot exist apparently to any appreciable extent in the presence of an MgX_2 compound, and it must have such an existence if Formula B ($R_2Mg{\cdot}MgX_2$) is correct.

However, all of the preceding discussion gives but a partial picture of things. In the first place, Gilman and Schulze[8] have presented convincing evidence for the following equilibrium with the related organoberyllium compounds

$$2RBeX \rightleftharpoons BeR_2 + BeX_2 \qquad \text{(V)}$$

Also, they called attention at that time to the probability of the same equilibrium with Grignard reagents, basing such a conclusion on the effect of heat on some Grignard reagents incidental to the preparation of ether-free crystalline organomagnesium halides.[9] Those experiments showed that Grignard reagents were converted to R_2Mg compounds on the application of heat.

$$2RMgX \longrightarrow R_2Mg + MgX_2 \qquad \text{(VI)}$$

The experiment with magnesium diethyl (previously referred to) shows that Reaction VI can also go from right to left. Since then we[10] have actually succeeded in distilling from the Grignard reagent (by a modification of the technique used by Gilman and Schulze[8] in the organoberyllium studies) the R_2Mg compound. In addition, the Experimental Part of this report contains an account of a second experiment with magnesium diethyl which may lend support to the following equilibrium

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad \text{(VII)}$$

All available evidence certainly confirms an equilibrium of this type with the RMgX form as the *chief* component of most Grignard reagents.

But this is not all. Some Grignard reagents undergo dissociation in the following manner

$$RMgX \longrightarrow R{-} + {-}MgX \qquad \text{(VIII)}$$

This is strikingly illustrated in the reaction between triphenylmethylmagnesium chloride, $(C_6H_5)_3CMgCl$, *free of metallic magnesium*, and benzophenone. In strict accordance with Reaction VIII the magnesious

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[8] Gilman and Schulze, This Journal, 49,2904 (1927); J. Chem. *Soc.*, 2663 (1927).

[9] Doctoral thesis of L. C. Heckert, Iowa State College, 1927.

[10] Gilman and Brown, *Rec. tmv. chim.*, 48, (1929). In confirmation of the reaction between magnesium diethyl and magnesium iodide to give ethylmagnesium iodide, Mr. Brown has shown that magnesium diphenyl with magnesium iodide gives phenylmagnesium iodide.

chloride[11] reduces benzophenone to benzopinacol, and the free radical or its equivalent (the peroxide) is formed. The dissociation postulated in Reaction VIII finds support in related unpublished studies. First, it is possible to prepare triphenylmethylmagnesium iodide from triphenyl methyl and magnesious iodide (—MgI).[12] This is, incidentally, a new method of theoretical interest for the preparation of Grignard reagents and lends support to earlier[13] experimental studies on the intermediate formation of free radicals in the preparation of Grignard reagents. Second, the molecular weight determinations of triphenylmethylmagnesium chloride and its reactions with hydrogen, oxygen and nitrous oxide lend further support to Reaction VIII.[14]

There is then a large amount of convincing evidence for both the equilibrium[15] represented by Reaction VII and the dissociation pictured by Reaction VIII. It remains to be determined to what extent the equilibrium and to what degree the dissociation takes place with a variety of Grignard reagents. From a purely theoretical basis it would be a relatively easy matter to assume that the equilibrium and the dissociation are properties of all Grignard reagents to *some* extent. Whatever results may come from future experiments, it is possible from the results of the present studies to have, as a working basis in the interpretation of some Grignard reactions, the postulate that Grignard reagents in solution may be a mixture of $RMgX$, R_2Mg, MgX_2, R— and —MgX in a series of equilibria.

[11] This does not appear to be in harmony with the statement that magnesium chloride does not react with magnesium to give magnesious chloride, an experiment verified by us. It may be argued that if Reaction VIII is correct, then a Grignard reagent like triphenylmethylmagnesium chloride should go irreversibly to form triphenylmethyl, magnesium and magnesium chloride, inasmuch as the magnesious chloride should (in accordance with Reaction I) proceed irreversibly to give the sparingly soluble magnesium chloride. But because such a reaction (leading to the formation of triphenylmethyl, magnesium chloride and magnesium) appears not to take place, one may conclude that the respective equilibria and rates of reaction are such as to make Reaction VIII a correct expression of the state of things under our experimental conditions. In this connection attention should also be directed to Menschutkin's studies [*Z. anorg. Chem.*, **49,** 34, **207** (1906)] on the tendency of magnesium halide etherates to form metastable supersaturated solutions.

[12] Studies by J. H. McGlumphy.

[13] Gilman and Fothergill, THIS JOURNAL, 50, **3334 (1928);** Gilman and Kirby, *ibid., 51,* **1571 (1929).** See, also, an earlier theoretical consideration by Gomberg and Bachmann, ibid., **49,236 (1927).** and Pickens, *Science,* **62,226 (1925).**

[14] Studies by J. **A.** Leermakers, a preliminary account of which was presented at the Iowa Academy of Science Meeting held at Fairfield, Iowa, in April **1929.** See, also, Gilman and Pickens, *Science,* **62, 220** (1925), and Gilman and Heck, Ber., **62, 1379** (1929).

[15] See, also, Grignard, *Compt. rend.,* 185, **507 (1927);** *Bull. soc. chim., 41,* **759** (1927), and the elegant studies that have just been published by Schlenk and Schlenk, *Ber.,* 62, 920 **(1929).**

Experimental Part

The primary objective of the several experiments was to isolate the benzopinacol[16] from other reaction products. After preparing the Grignard reagent in the customary manner, another equivalent of magnesium turnings and 50 to 100 cc. of dry benzene were added. We used magnesium turnings because preliminary experiments showed that the yield of benzopinacol prepared from such turnings and iodine and benzophenone was equal to the yield of benzopinacol obtained when magnesium powder was used. Gomberg and Bachmann[4] have shown that the rate of reaction is more rapid with magnesium powder.

The calculated quantity of a benzene solution of benzophenone was added with stirring to the cooled solution of Grignard reagent and the heat of reaction was generally great enough to cause the ether–benzene solution to reflux. External heat was not applied in any of the experiments. After adding the benzophenone, the reaction mixtures were stirred or shaken vigorously for varying lengths of time. In long runs when the flask was not tightly stoppered an inert atmosphere was used.

At the conclusion of an experiment, any precipitate that formed was allowed to settle, the clear supernatant solution was decanted and to this solution was added an ether–benzene washing of the precipitate. The solution and the precipitate were hydrolyzed separately, first with water and then with dilute hydrochloric acid.[17]

The acid layers were extracted once or twice with an ether–benzene mixture, and the combined extract and ether–benzene layers were dried with anhydrous sodium sulfate, after which the solvents were removed by distillation from a water-bath followed by a current of dry air. The residues from the solution and from the precipitate were then extracted with 100 to 200 cc. of petroleum ether (40–60°), and after this treatment benzopinacol remained.[18] If the precipitate of the reaction mixture were

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[16] Others have obtained benzopinacol from the reaction between benzophenone and the Grignard reagent. Actually it was the formation of benzopinacol from a reaction between benzophenone, magnesium and an aryl halide that led Gomberg and Bachmann[4] to a study of magnesious halides. Prior to that time, Schmidlin, *Ber.*, **39**, 4198 (1906), obtained benzopinacol from benzophenone, triphenylmethylmagnesium chloride and an excess of magnesium. Subsequently Lagrave, *Ann. chim.*, [10] 8, **363** (1927), isolated small quantities of benzopinacol from benzophenone and various Grignard reagents. He very correctly attributed the formation of the small quantities of benzopinacol to a secondary reaction between some magnesium iodide and a slight excess of magnesium.

[17] Any unused magnesium in the precipitate was removed prior to the acid hydrolysis.

[18] Benzopinacol is partly soluble in petroleum ether. This was shown in a thirteen-hour extraction of 10 *g.* of benzopinacol in a Soxhlet extractor by 150 cc. of petroleum ether. Two and four-tenths grams of benzopinacol was dissolved in this way. Accordingly, our yields of benzopinacol are, in some cases, slightly less than those actually

not washed well with the ether–benzene mixture, some of the halogen-magnesium pinacolate (dissolved in the ether–benzene mixture) would remain with the precipitate (the halogen-magnesium tertiary alcoholate) and a mixture of pinacol and tertiary alcohol, $R(C_6H_5)_2COH$, would result on hydrolysis. This small quantity of pinacol can be separated largely from the tertiary alcohol by dissolving the mixture in hot glacial acetic acid; then, on cooling, the pinacol crystallizes first.

In those experiments concerned with the dissociation of the Grignard reagent, the reagent was prepared in the usual manner and then filtered through cotton or glass wool packed in a tube.[19] The benzophenone was then added to the filtered solution of the Grignard reagent and the reaction carried out and worked up as previously described.

A general account of the results of the several experiments is given in Table I and particular details and comments are included in the footnotes accompanying it.

Magnesium Diethyl, Magnesium Iodide and Magnesium.—The magnesium diethyl was prepared by heating 38.9 g. (0.15 mole) of mercury diethyl with 7.3 g. (0.3 atom) of magnesium turnings in a sealed tube at 100–120° for thirty-six hours. The magnesium iodide solution was prepared[4] from 14.6 g. of magnesium and 38.1 g. of iodine. All transferals and operations were carried out in a special apparatus and in a stream of dry and pure hydrogen. There was little evidence of reaction when the ether solution of magnesium diethyl was added to the magnesium iodide and magnesium. After adding 109.2 g. (0.6 mole) of benzophenone in 100 cc. of benzene, stirring was continued for five hours and then the mixture was allowed to settle overnight. The pink supernatant solution yielded 1.3 g. or 1.18% of benzopinacol.

Inasmuch as a deep pink color formed near the particles of magnesium, more solvent was then added and the precipitate was stirred intermittently, for an additional twenty-five hours, during a total time of one hundred hours. The red solution was then decanted and worked up separately from the precipitate. This solution yielded 7.8 g. or 7.1% of benzopinacol. Crystallization of the products obtained from the precipitate gave 5.0 g. of benzopinacol and 20.1 g. of ethyldiphenylcarbinol. The total yield of benzopinacol, based on benzophenone, was 14.1 g. or 12.83%.[20]

In a second experiment an atmosphere of nitrogen was used and the reaction mixture was stirred for only one-half hour subsequent to addition of benzophenone, and then hydrolyzed. No benzopinacol was obtained from the yellow solution of the reaction mixture and the yield of ethyldiphenylcarbinol was 22.9 g. or 18.0%.

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present. Also, it must be remembered that we are dealing here with mixed solvents, because the benzopinacol is being extracted not only by petroleum ether but also by any benzophenone and tertiary alcohol dissolved by the petroleum ether. The Soxhlet extractor was used only in the benzylmagnesium chloride experiment.

[19] Another way of filtering solutions from magnesium is to use a matte of sintered glass fused into a glass tube. Such a filter has been used by Gilman and Brown in their studies on magnesium dialkyls and diaryls (see ref. 10 of this paper).

[20] There are several possible explanations for the formation of benzopinacol in this long-time run. One of them involves the following reaction: $2(C_6H_5)_2(C_2H_5)\text{-}COMgI \longrightarrow ((C_6H_5)_2(C_2H_5)C\text{—}O)_2Mg + MgI_2$. The magnesium iodide thus formed would react with the magnesium present to give magnesious iodide, which in turn would reduce the benzophenone to benzopinacol.

TABLE I
REACTANTS AND PRODUCTS

	Reactants				Products				
					Benzopinacol				
Expt.	RMgX	Mole	Mg, g. atom	Benzophenone, mole	G.	%	Tertiary alcohol	G.	%
1	CH_3MgI[a]	0.2	0.2	0.4	0.04	0.057	$(C_6H_5)_2(CH_3)COH$	22.1	27.9
2	CH_3MgI[b]	.3	.3	.3	2.0	3.6	$(C_6H_5)_2(CH_3)COH$	48.3	81.3
3	C_2H_5MgCl[c]	.3	.3	.3	0.0	0.0	$(C_6H_5)_2(C_2H_5)COH$	2.85	4.5
4	*n*-C_4H_9MgI[d]	.3	.3	.3	5.5	10.0	$(C_6H_5)_2(C_4H_9)COH$	21.0	36.3
5	*n*-C_4H_9MgI[e]	.3	.3	.3	9.5	17.3	$(C_6H_5)_2(C_4H_9)COH$	15.1	26.1
6	*n*-C_4H_9MgI[f]	.2	.0	.2	0.0	0.0	......	..	..
7	*tert.*-C_4H_9MgCl[g]	.3	.0	.3	0.0	0.0	......	..	..
8	C_6H_5MgBr[h]	.2	.2	.4	0.0	0.0	$(C_6H_5)_3COH$	38.5	36.9
9	C_6H_5MgBr[i]	.3	.3	.3	Trace	Trace	$(C_6H_5)_3COH$	61.9	79.3
10	$C_6H_5CH_2MgCl$[j]	.3	.3	.3	0.0	0.0	$(C_6H_5)_2(C_6H_5CH_2)COH$	70.0	85.2
11	$C_6H_5CH_2MgBr$[k]	.2	.2	.4	0.55	0.75	$(C_6H_5)_2(C_6H_5CH_2)COH$	10.4	9.5
12	$C_6H_5CH_2MgBr$[l]	.25	.0	.25	0.0	0.0	$(C_6H_5)_2(C_6H_5CH_2)COH$	35.0	51.0
13	$(C_6H_5)_3CMgCl$[m]	.03	.0	.043	1.73	22.0	$(C_6H_5)_2((C_6H_5)_3C)COH$	1.0	7.8
14	$(C_6H_5)_3CMgBr$[n]	.03	.0	.043	2.49	31.6	$(C_6H_5)_2((C_6H_5)_3C)COH$	0.55	4.3

[a] All of the yields given in Table I are based on the quantity of benzophenone taken for each experiment. Unless otherwise stated iodine was not used as a catalyst in the preparation of the several Grignard reagents. The diphenylmethylcarbinol, $(C_6H_5)_2(CH_3)COH$, and unused benzophenone formed an oil that did not separate well by fractional crystallization from petroleum ether. It was partly for this reason that the excess of benzophenone was not used in many of the other experiments. Where such an excess was not used, the results, of course, are not of the same accuracy as in the other experiments where an excess was used. However, the differences at best are very slight in those experiments carried out with a selected Grignard reagent and with and without an excess of benzophenone (*cf.* Expts. 1 and 2, 8 and 9). Actually, from these comparative experiments (1 and 2, 8 and 9) more benzopinacol was isolated when the excess of benzophenone was not used. In this experiment the mixture was stirred for one hour prior to hydrolysis. There was no red color in the solution at the end of addition of ketone and the whitish precipitate was tinged slightly with a greenish yellow color. When about one-half of the ketone had been added there was a faint red color.

[b] In this run with methylmagnesium iodide, the solution took on a reddish color and the red precipitate which formed did not diminish appreciably after shaking for twenty minutes. As with all other solid products isolated in this study, the identity of the benzopinacol was confirmed by a mixed melting-point determination with an authentic specimen.

[c] The addition of benzophenone in **50** cc. of benzene to the ethylmagnesium chloride and magnesium caused the formation of a white precipitate. An orange color formed momentarily at the spot of addition of benzophenone but when all of the ketone had been added no color was left in the solution. The mixture was stirred for one hour prior to hydrolysis.

[d] A white precipitate formed and the solution was of a purple color. Stirring was continued for three hours after the addition of ketone and at the end of the three-hour period the solution had become a pink color. From the precipitate of the reaotion mixture there were obtained **15.1** g. or 27.4% of crude benzohydrol, $(C_6H_5)_2CHOH$, melting at **64–65'**, and **9.3** g. or 17.8% of dibenzohydryl ether, $((C_6H_5)_2CH)_2O$. In all of the experiments with n-butylmagnesium iodide, a vacuum distillation was carried out with the oil that did not crystallize from petroleum ether. The dibenzohydryl ether may owe its formation to the effect of heat on benzohydrol and benzopinacol.

[e] This experiment was like Expt. No. 4, excepting that n-butylmagnesium iodide was prepared by the *rapid* addition of butyl iodide to magnesium in ether, thus favoring the greater formation of magnesium iodide as a side-product.

Part of the benzopinacol (**5.0** g. or **9.1**%) came from the solution, and the remainder was obtained from the precipitate as **19.9** g. of a solid which melted between **66** and 160° and which proved to be a mixture of benzopinacol and benzohydrol. An attempt was made to separate this mixture by converting the benzopinacol in it to benzopinacolone hy the method of Gomberg and Bachmann,[4] which involves boiling the pinacol in glacial acetic acid for a few minutes with a trace of iodine. On cooling the acetic acid solution, there separated pure benzopinacol instead of the expected benzopinacolone. In this manner the mixtnre gave **4.5** g. of benzopinacol and **15.4** g. of benzohydrol.

[f] In this third run with *n*-butylmagnesium iodide the object was to determine whether there was any dissociation of the Grignard reagent. Accordingly, the ketone was added to a filtered solution of n-butylmagnesium iodide free of magnesium. A white precipitate formed and the solution turned brown with a trace of pink, which may have been indicative of some reduction of the benzophenone. The mixture was stirred for three hours and among the reaction products was **9.9** g. or 26.9% of benzohydrol which melted at **67–68**" and which was obtained from the precipitate portion of the reaction mixture. The tertiary alcohol from this experiment was not worked up.

[g] In a first experiment with *tert.*-butylmagnesium chloride, the Grignard reagent was prepared by the use of a bare trace of iodine as a catalyst. Because this experiment was carried out to determine whether any dissociation occurred, the Grignard solution was filtered through a funnel packed with glass wool. The solution took on a red color and the precipitate which formed did not dissolve after shaking for a few minutes. The quantity of benzopinacol formed was **0.45** g. or **0.98%.** By a vacuum distillation of the residues left after evaporation of the petroleum ether solutions of both parts of the reaction mixture, there was obtained **30.6** g. or **63.7%** of an oil distilling at 147–165° (4 mm.). This was probably *tert.*-butyldiphenylcarbinol or dehydration products. In the experiment listed as No. 7 in Table I, no iodine was used as a catalyst and the Grignard solution was filtered through a plug of cotton instead of glass wool. **A** white precipitate formed and with it a reddish colored solution which gradually changed to greenish yellow. No benzopinacol was isolated. Some benzophenone (**2.4** g.) was recovered. Nothing was done with the tertiary alcohol fraction in this experiment.

[h] In this experiment with phenylmagnesium bromide, stirring was continued for two hours after addition of the ketone. The solution containing a white precipitate was of a yellow color prior to hydrolysis. In this experiment, as in the others in which an excess of benzophenone was used, there was a residue composed of a mixture of tertiary alcohol and benzophenone which did not lend itself to ready separation by means of

fractional crystallization from petroleum ether. The quantity of benzophenone recovered was **25.4** g. or **34.87,.**

[i] stirring was continued for three hours in this run and the trace of benzopinacol isolated is very probably due to the trace of iodine used in the preparation of the phenylmagnesium bromide. The trace of benzopinacol was obtained from 1.7 g. of a solid (melting at 145–150°) which was separated from the solution part of the reaction mixture. It was obtained in a pure condition by recrystallization From a mixture of alcohol and chloroform, followed by two crystallizations from glacial acetic acid.

[j] On the first addition of benzophenone to the benzylmagnesium chloride prepared with a trace of iodine, **a** small quantity of white precipitate formed; this dissolved completely by the time all of the ketone had been added. The faint lavender colored solution was stirred for one hour and then worked up in the usual manner. The benzyldiphenylcarbinol was not very soluble in petroleum ether, so that any small quantity of benzopinacol could not be isolated by extraction with **300** cc. of petroleum ether. **A** 3.5-hour extraction with 250 cc. of petroleum ether in a Soxhlet extractor failed to separate any benzopinacol (see ref. **18). A** recrystallization of a portion of the tertiary alcohol from glacial acetic acid gave no trace of benzopinacol.

[k] The mixture was stirred for four hours and the yellowish solution present prior to hydrolysis contained a white precipitate. The quantity of benzophenone recovered was **38.5** g. or 52.9%.

[l] In this experiment the object was to determine whether benzylmagnesium bromide dissociated. On adding the benzophenone to the filtered Grignard solution, a momentary purple color formed at the spot of addition and when all of the ketone had been added the solution was of a yellow-brown color. No precipitate formed. **A** recrystallization of a part of the benzyldiphenylcarbinol from glacial acetic acid gave no benzopinacol.

[m] The triphenylmethylmagnesium chloride and bromide, respectively, used in Expts. **13** and 14 were prepared in accordance with the directions of Gilman and Zoellner, THIS JOURNAL, 51, NOV. **(1929).** When benzophenone in benzene was added to the filtered benzene solution of Grignard reagent an intense red color formed. The solution was shaken for a few minutes and then hydrolyzed. In addition to the products listed in Table I, there was obtained **4.3** g. or 55.3% of triphenylmethyl peroxide. There was an excess of benzophenone because a small quantity of it was recovered directly from the petroleum ether extract of the crude pinacol. This experiment was carried out in a nitrogen atmosphere.

[n] This experiment was like that with the triphenylmethylmagnesium chloride. The yield of triphenylmethyl peroxide was **4.5** g. or **57.9%.** Evidently there was an excess of benzophenone because a portion of the petroleum ether extract of the crude pinacol gave some benzophenone-oxime when treated in the customary manner with hydroxylamine. This experiment was carried out in a nitrogen atmosphere.

Summary

Evidence is presented for the following equilibrium, $2RMgX \rightleftarrows R_2Mg + MgX_2$, and the following dissociation, $RMgX \longrightarrow R- + -MgX$, of Grignard reagents.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OB THE UNIVERSITY OF NEBRASKA]

N-PHENYL-BETA-AMINOPROPIONAMIDE-4-ARSONIC ACID AND RELATED COMPOUNDS

BY CLIFF S. HAMILTON AND CARTER L. SIMPSON

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The comparatively recent preparation of "tryparsamide," N-phenylglycine-amide-4-arsonic acid[1] and its growing use in trypanosomiasis and neuro-syphilis stimulated an interest in the preparation and study of other arsenicals of a similar structure which might be more efficient. Those which merited special interest were the two compounds corresponding to tryparsamide, one having an additional methylene group in the side chain and the other having a shorter side chain.

The method employed in the preparation of "tryparsamide" involved the condensation of p-arsanilic acid with chloro-acetamide and subsequent conversion into the monosodium salt. N-Phenyl-β-aminopropionamide-4-arsonic acid was prepared by refluxing a neutral solution of sodium p-arsanilate with either β-bromopropionamide or with β-iodopropionamide. The monosodium salt was obtained by dissolving the acid in a sodium hydroxide solution and filtering into absolute alcohol. Attempts to prepare 4-carbamido-phenylarsonic acid by the action of carbamyl chloride on p-arsanilic acid were unsuccessful. However, N-4-methylcarbamidophenylarsonic acid[2] was prepared by the action of methylcarbamyl chloride on p-arsanilic acid. This compound was first prepared from methyl isocyanate and p-arsanilic acid. β-iodopropionamide was also condensed with several other amino-arylarsonic acids.

It was of interest also to make a study of an unsymmetrical arseno compound, composed of a half molecule of arsphenamine, used in the treatment of primary syphilis, and a group somewhat similar to tryparsamide, of benefit in neuro-syphilis. 3-Amino-4-hydroxy-4'-propionamideamino-arsenobenzene resulted when molecular equivalents of 3-amino-4-hydroxyphenylarsonic and N-phenyl-β-aminopropionamide-4-arsonic acid were condensed, using hypophosphorous acid as the reducing agent.

A detailed study of the pharmacological action of N-phenyl-β-aminopropionamide-4-arsonic acid is now being carried out in the Department of Pharmacology, University of Wisconsin. Preliminary results indicate that it may be useful in trypanosomal infections.

Experimental Part

β-Bromopropionyl Chloride.—Twenty *g*. of β-bromopropionic acid and 10 cc. of phosphorus trichloride were heated under a reflux condenser on a water-bath for five hours. The pale straw-colored liquid was collected at 65–70° at 25–30 mm.; yield, 19.6 g.

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[1] Jacobs and Heidelberger, THIS JOURNAL, 41, 1589 (1919).

[2] Farb. Meister, Lucius and Bruning, German Patent 213,155.

Anal. Subs., 0.2001, 0.2004. Calcd., 0.3865, 0.3871 g. of silver halide. Found: 0.3854, 0.3862.

β-Iodopropionyl Chloride.—This was obtained in 80% yields, being collected at 85–90' and 30 mm.

β-Bromopropionamide.—Sixteen g. of β-bromopropionyl chloride was admitted drop by drop with rapid stirring to a solution of 21 cc of concentrated ammonium hydroxide diluted to 35 cc. and kept at −10°. The white crystalline amide separated and after stirring the mixture for a short time it was filtered and washed with a small amount of ice water to remove ammonium chloride; yield, 11.2 g.; m. p. 110–111°. For analysis the product was recrystallized twice from hot water.

Anal. Subs., 0.4005, 0.4011: 2G.1, 26.3 cc. of 0.1 N HCl. Calcd.: X, 9.21. Found: N, 9.13, 9.17.

β-Iodopropionamide.—This compound was prepared in 80% yields by following the method of Jacobs and Heidelberger.[3]

N-Aryl-β-aminopropionamide-arsonic Acids

General Method of Preparation.—One molecular equivalent of the amino-arylarsonic acid was dissolved in the calculated amount of normal sodium hydroxide solution to form a monosodium salt; one and one-half molecular equivalents of the halopropionamide was then added and the mixture boiled under a reflux condenser for five hours. Sufficient concentrated hydrochloric acid was added to the hot solution to hold any unchanged arsanilic acid in solution. The solution deposited almost colorless crystals on cooling. The product was filtered, washed with a little cold water and purified by dissolving in 2 N sodium hydroxide solution, filtering and reprecipitating by the addition of concentrated hydrochloric acid. This purification was repeated until the product gave a negative R-salt test.

β-Bromopropionamide and β-iodopropionamide were the two halopropionamides used in the preparation of the N-aryl-β-aminopropionamide-arsonic acids. Of these the β-bromo compound was found to give the better results, the crude products being whiter and the yields just as high as when β-iodopropionamide was used.

TABLE I

N-ARYL-β-AMINOPROPIONAMIDE-ARSONIC ACIDS

N-Phenyl-β-amino-propionamide-( )-arsonic acid	Formula	Yield, %	Subs., g.	Analysis 0.0497 *N* I2, cc.	Analysis Arsenic, % Calcd.	Analysis Arsenic, % Found
-4-	$NH_2CO(CH_2)_2NHC_6H_4AsO_3H_2$	35–40	0.2060	28.52	26.04	26.00
-2-Methyl-5-	$NH_2CO(CH_2)_2NHC_6H_3(CH_3)AsO_3H_2$	15–20	.2016	26.6	24.73	24.60
-2-Methyl-4	$NH_2CO(CH_2)_2NHC_6H_3(CH_3)AsO_3H_2$	25–30	.2034	26.8	24.73	24.54

Monosodium Salt of N-Phenyl-β-aminopropionamide-4-arsonic Acid.—This was prepared by dissolving N-phenyl-β-aminopropionamide-4-arsonic acid in the calculated amount of 2 N sodium hydroxide solution to give a neutral solution and filtering in a fine stream into 10 volumes of absolute alcohol, previously cooled to 0°. The mixture was allowed to stand for several hours in a freezing bath to insure complete precipitation. The sodium salt separated in fine white needles containing approximately two moles of water of hydration. The yield was almost quantitative.

Anal. (Sample dried at 110°) Subs., 0.2245; 29.33 cc. of 0.0497 N I_2. Calcd. for $C_9H_{12}O_4N_2AsNa$: As, 24.19. Found: As, 24.20. (Sample air dried) Subs., 0.2016:

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[3] Jacobs and Heidelberger, J. *Biol. Chem.*, *21*, 145 (1915).

23.90 cc. of 0.0497 N I_2. Calcd. for $C_9H_{12}O_4N_2AsNa2H_2O$: As, 21.68. Found: As, 21.90.

N-Phenyl-β-aminopropionic Acid-Carsonic Acid.—Five g. of N-phenyl-6-aminopropionamide-4-arsonic acid was gently boiled under a reflux condenser with 50 cc. of 2 N sodium hydroxide solution for three hours, or until ammonia ceased to be evolved. The solution deposited fake-like crystals when made acid to Congo Red paper with concentrated hydrochloric acid and cooled in a freezing mixture; yield 4.5 g. It did not melt below 250°.

Anal. Subs., 0.2019, 0.2012; 28.1, 27.9 cc. of 0.0497 N I_2. Calcd. for $C_9H_{11}O_4NAs$: As, 26.04. Found: As, 25.92, 25.83.

N-4-Methyl-carbamido-phenylarsonic Acid.—Five g. of methylcarbamyl chloride, prepared by treating methylamine hydrochloride with phosgene at 250–300°, was dissolved in 30 cc. of dry benzene and cooled to 5°. Five g. of finely powdered sodium *p*-arsanilate was then added in small portions with shaking. In order to complete the reaction the temperature of the mixture was allowed to rise slowly to 20°. The resulting product was then filtered, washed repeatedly with benzene and finally with ether. It was then triturated with water to remove the hydrochloride formed in the reaction and recrystallized from hot water; yield, 25%.

Anal. Subs., 0.2004: 29.50 cc. of 0.0497 N I_2. Calcd. for $C_8H_{11}O_4N_2As$: As, 27.37. Found: As, 27.44.

Arseno Compounds

3-Amino-4-hydroxy-4′-propionamidamino-arsenobenzene Dihydrochloride.—A mixture of 4.7 g. of 3-amino-4-hydroxyphenylarsonic acid and 5.8 g. of N-phenyl-0-aminopropionamide-4-arsonic acid was dissolved in a solution of 50 cc. of concd. hydrochloric acid and 30 cc. of water. Fifty cc. of 50% hypophosphorous acid was then added and the solution kept in a refrigerator for twenty-four hours. The yellow precipitate was filtered, washed with alcohol, then with ether and dried in a vacuum; yield, 4.2 g. The compound was soluble in water.

Anal. Subs., 0.2012, 0.2005: 32.0, 31.9 cc. of 0.0501 N I_2. Calcd. for $C_{15}H_{19}O_2N_3Cl_2As_2$: As, 30.36. Found: As, 29.88, 29.89.

In order to prepare the free base, the dihydrochloride was dissolved in water and 3-amino-4-hydroxy-4′-propionamidamino-arsenobenzene precipitated by the careful addition of a sodium hydroxide solution. The free base was also prepared as follows: one hundred g. of sodium hydrosulfite was added with stirring to a solution of 21.2 g. of magnesium chloride hexahydrate in 500 cc. of water. To this was then added 3.6 g. of 3-amino-4-hydroxyphenylarsonic acid and 4.6 g. of N-phenyl-β-aminopropionamide-4-arsonic acid, dissolved in 160 cc. of water containing 20 cc. of a saturated sodium carbonate solution. The mixture was filtered as quickly as possible and warmed at 50° for one hour. The free base separated as a yellow, insoluble powder, which was filtered, washed with water and immediately dried in a vacuum; yield, 5.5 g. It decomposed at 120–125° and contained a small amount of sulfur as an impurity.

Anal. Subs., 0.2006: 38.44 cc. of 0.0497 N I_2. Calcd. for $C_{15}H_{17}O_2N_3As_2$: As, 35.63. Found: As. 35.01.

Summary

1. N-Phenyl-P-aminopropionamide-4-arsonic acid and its sodium salt have been prepared. Preliminary pharmacological tests indicate that it may be useful in treatment of trypanosomal infections.

2. β-Bromopropionyl chloride, β-bromopropionamide, N-phenyl-β-

aminopropionamide-2-methyl-5-arsonic acid and N-phenyl-β-propionamide-2-methyl-4-arsonic acid have been described for the first time.

3. 3-Amino-4-hydroxy-4'-propionamido-arsenobenzene and its hydrochloride have been prepared.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

NEW CONDITIONS FOR THE FORMATION OF GLUCOSAZONE

BY C. L. BUTLER AND LEONARD H. CRETCHER

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Hydrazine derivatives of recently described compounds in which uronic acids are conjugated with sugars[1] have not yet been studied. We desired to prepare such derivatives of the aldobionic acid isolated from gum arabic[1b] in order further to characterize it. While a number of hydrazine derivatives of glucuronic acid have been prepared, the lack of agreement in the results of various investigators in this field seems to indicate that the reaction is not a simple one.[2]

A preliminary investigation of the action of phenylhydrazine on the simpler sugars, glucose, mannose and fructose was therefore made. The chemistry of glucose phenylhydrazone[3] is complicated by the existence of at least two isomeric forms. Although we have spent a considerable amount of time attempting to prepare the pure isomers, our results indicated that these are not readily produced by any of the published methods. Since our results were not conclusive, further discussion in this paper will be confined to a description of the formation of glucosazone from glucose and fructose, and from their phenylhydrazones under conditions not ordinarily considered favorable to osazone formation, and of the behavior of mannose phenylhydrazone under similar conditions.

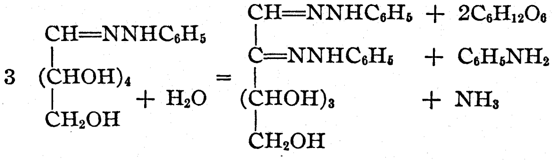
The precipitation of glucosazone from a cold dilute acetic acid solution of 1 equivalent of glucose and 1.5 equivalents of phenylhydrazine was observed by Jacobi.[3c] This investigator did not examine the reaction further. It was found in the present work that when glucose is treated under

[1] (a) Heidelberger and Goebel, *J. Biol. Chem.*, **74**, 613, 619 (1927); (b) Butler and Cretcher, THIS JOURNAL, **51**, 1519 (1929); (c) see also Anderson and Sands, *ibid.*, 48, 3172 (1926).

[2] References to the literature of this subject may be found in (a) Van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydesäuren," Gebrüder Borntraeger, Berlin, **1920**, Chapter VI, and in (b) Tollens, "Kurzes Handbuch der Kohlenhydrate," Earth, Leipzig, **1914**, pp. 766–767.

[3] (a) Fischer, *Ber.*, 20, 824 (1887); (b) Skraup, *Monatsh.*, **10**, 406 (1889); (c) Jacobi, *Ann.*, **272**, 172 (1892); (d) Simon and Eenard, Compt. rend., **132**, 564 (1901); (e) Behrend, *Ann.*, **353**, 106 (1907); (f) Behrend and Lohr, *ibid.*, 362, 78 (1908); (g) Behrend and Reinsberg, *ibid.*, **377**, 189 (1911).

similar conditions with an equimolecular proportion of phenylhydrazine, a precipitate of glucosazone is formed after a few hours. On prolonged standing a 62.5% yield of glucosazone, based on the amount of phenylhydrazine used, was obtained. In the absence of acetic acid this reaction did not take place.[4] No other crystalline product could be isolated from the mother liquors. It was also shown that glucose phenylhydrazone itself, when allowed to stand at room temperature in dilute acetic acid, changes to glucosazone. The yield was 85% based on the equation



$$3\begin{array}{l}CH{=}NNHC_6H_5\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} + H_2O = \begin{array}{l}CH{=}NNHC_6H_5\\ |\\ C{=}NNHC_6H_5\\ |\\ (CHOH)_3\\ |\\ CH_2OH\end{array} \begin{array}{l}+ 2C_6H_{12}O_6\\ + C_6H_5NH_2\\ + NH_3\end{array}$$

The formation of glucosazone under these conditions probably involves an intramolecular oxidation and reduction the mechanism of which will not be discussed in the present paper. That this is also the main reaction in alcoholic solutions of glucose and phenylhydrazine containing acetic acid was shown by the isolation of a 63% yield of glucosazone on attempting to repeat the preparation[3f] of Behrend's glucose a-phenylhydrazone. It was not possible to isolate any hydrazone from the glucosazone mother liquors.

Attempts to prepare crystalline fructose phenylhydrazone were unsuccessful. The reaction product in the absence of solvent was a gummy mass which could not be crystallized. However, equimolecular proportions of fructose and phenylhydrazine in dilute acetic acid at room temperature gave a 67% yield of glucosazone. The gummy reaction product of fructose and phenylhydrazine also changed to glucosazone when treated in a similar manner.

Mannose phenylhydrazone was found to be stable under these conditions. However, when warmed in dilute acetic acid it gave rise to black resinous material which could not be purified. That mannose was liberated in this reaction was shown by the fact that the mother liquor, after removal of the resinous material by filtration, deposited mannose phenylhydrazone on treatment with phenylhydrazine.

Experimental

Attempted Preparation of Glucose Phenylhydrazone by the Method of Behrend and **Lohr.**[3f]—To a solution of 20 g. of glucose in 15 g. of glacial acetic acid and 5 cc. of water was added a solution of 15 g. of phenylhydrazine in 160 cc. of absolute alcohol. On thorough mixing a clear yellow solution was obtained. After standing for three days 10.5 g. of crude yellow crystals was filtered from the solution. On washing with acetone 7.5 g. of bright yellow crystals, melting at 206–207°, was obtained. The

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[4] Cameron, THIS JOURNAL, 48, 2233 (1926), has noted the effect of acetic acid as a catalyst in the reaction of weak bases such as aniline with glucose. His conclusions are confirmed by the experiments herein reported.

mother liquor from these crystals was allowed to stand for two days, and deposited during this time a further quantity of crystalline material which after washing with acetone weighed 2.0 g. One additional gram of crystals was recovered from the mother liquors on concentration *in vacuo* to about 60 cc. This material was recrystallized from 70% alcohol. The purified substance, which melted at 210°, did not depress the melting point of an authentic sample of glucosazone which melted at 210°. The total yield of glucosazone was 10.5 g. or 63.2% of the theoretical based on the amount of phenylhydrazine used.

Preparation of Glucose Phenylhydrazone by the Method of **Fischer.**[3a]—The yield from 5 g. of glucose. 5 g. of phenylhydrazine and 2.5 g of water was 4.5 g or 60% of the theoretical of hydrazone melting at various temperatures between 140 and 150°. On addition of ether to the concentrated sirupy mother liquor, 1.7 g., or 22.7% of the theoretical of Skraup's phenylhydrazone[3b] melting at 111–112° was obtained. The total hydrazone yield was thus 6.2 g. or 82.7% of the theoretical.

A modification of this method was tried in the hope of obtaining the glucose α-phenylhydrazone of Behrend. To a suspension of 18 g. of glucose in 6 cc. of water and 25 cc. of absolute alcohol was added a solution of 11 g. of phenylhydrazine in 25 cc. of absolute alcohol. The resulting clear solution was allowed to stand overnight at room temperature and then for several days in the ice box. The crystalline mass was filtered and the crystals were washed with ether. The material was then precipitated several times from alcohol solution by ether. The yield was 17 g. of Skraup's phenylhydrazone melting at 110–112°, or 63% of the theoretical.

Preparation of **Mannose Phenylhydrazone.**—This compound was prepared from 3.6 g. of mannose and 2.2 g. of phenylhydrazine in the usual way. The yield was 4.8 g. (89% of the theoretical) of pure mannose phenylhydrazone melting at 200–201°.

Attempted Preparation of Fructose **Phenylhydrazone.**—The method of Laudrieu[5] applied to the production of fructose phenylhydrazone gave unsatisfactory results. The preparation was therefore attempted without solvent. To 1.8 g. of fructose was added 1.8 g. of phenylhydrazine and the mixture was stirred until uniform. It was allowed to stand at room temperature for forty-eight hours. The sticky mass was extracted with ether to remove the excess of phenylhydrazine. On drying about 1.5 g. of a soft gummy mass was obtained. It could not be crystallized.

Preparation of Glucosazone.—Glucosazone was prepared by the usual method. The substance purified by crystallization from 60% alcohol and washing with acetone melted at 210°. The melting point was not changed by recrystallization from 60% alcohol; α^{20}_{D} $-2.625''$ for $l = 2$ and $c = 2$, ten minutes after solution in a mixture of 1 part of pyridine and 1.5 parts of alcohol; $[\alpha]^{20}_{\mathrm{D}\,(\mathrm{initial})}$ $-65.6°$. The rotation became constant after twenty-five hours at $-1.44°$; $[\alpha]^{20}_{\mathrm{D}\,(\mathrm{final})}$ $-36.0°$.

The Formation of Glucosazone from Equimolecular Proportions of Glucose **and Phenylhydrazine.**—Thirty-six g. of glucose was dissolved in 200 cc. of water and to the solution was added a mixture of 50 cc. of water, 10 cc. of glacial acetic acid and 21.6 g. of phenylhydrazine. The resulting milky suspension was allowed to stand at room temperature. The following day a large amount of yellow crystalline solid had separated. The amount of solid increased on standing. After six days the material was filtered off and washed with a little water. It melted at 183° with decomposition. The crude product, when purified as described above, melted at 209–210°. Six g. of bright yellow crystals was obtained in this crop. The filtrate from the crude crystals, on standing for several weeks longer, deposited a further quantity of glucosazone which after purification weighed 7 g.

The combined mother liquors were concentrated to about 30 cc. in *vacuo* and diluted

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[5] Landrieu, Comfit. *rend.,* 142, 182 (1906).

with an equal volume of alcohol. Water was then added until no further precipitation occurred and the mixture was filtered. The crude solid material on purification yielded two additional grams of pure osazone. The total yield was thus **15** g. of pure substance or **62.5%** of the theoretical based on the equation given in the first part of this paper. The substance did not depress the melting point of pure glucosazone prepared as described above; $[\alpha]^{20}_{\mathrm{D}\ (\text{initial})}$ $-56.3°$ for $c = 2$ and $l = 2$; $[\alpha]^{20}_{\mathrm{D}\ (\text{final})}$ $-36\ 5°$.

A control experiment in which **1.8** g. of glucose was treated with **1.1** g. of phenylhydrazine in **12.5** cc. of water in the absence of acetic acid was made. No precipitate of glucosazone was formed after standing for two days at room temperature.

Formation of Glucosazone from Glucose **Phenylhydrazone.**—One cc. of glacial acetic acid was added to a solution of **2** g. of Fischer's glucose phenylhydrazone in 10 cc. of cold water. The solution became cloudy after standing for two hours at room temperature. After standing overnight, a large amount of yellow insoluble material had separated from solution. The mixture was filtered ten days later. The yield was **0.75** g. of recrystallized glucosazone melting at 210° or 85% of the theoretical based on the equation given on page **3162.** The substance did not depress the melting point of a sample of pure glucosazone which melted at 210°.

The presence of glucose was demonstrated in the filtrate from the glucosazone precipitate by warming with a little phenylhydrazine and a few drops of acetic acid. The glucosazone which was formed was filtered off and purified in the usual way. It melted at **210°**.

A control experiment was run with **2** g. of glucose phenylhydrazone in **10** cc. of water without the addition of acetic acid. There was no glucosazone formation in this experiment.

Two grams of Skraup's phenylhydrazone was treated similarly. The yield of purified osazone melting at 210° was **0.7** g. or **80%** of the theoretical.

Formation of Glucosazone from Equimolecular Proportions of Fructose and **Phenylhydrazine.**—A suspension of **2.2** g. of phenylhydrazine in **5** cc. of water was added to a solution of **3.6** g. of fructose in **15** cc. of water and 1.5 cc. of acetic acid. The mixture became cloudy after several hours and after several days the deposition of glucosazone appeared to have ceased. The mixture was filtered and the glucosazone purified by methods which have been described. The yield was **1.6 g.** of pure glucosazone melting at **209–210°,** or **67%** of the theoretical.

Formation of Glucosazone from the Crude Reaction Product of Equimolecular Proportions of Fructose and **Phenylhydrazine.**—One g. of the sticky product was dissolved in **5** cc. of water and filtered from a trace of yellow insoluble material. Several drops of acetic acid were added and the mixture was allowed to stand for two days at room temperature. The yield of pure glucosazone melting at 210° was **0.35** g. or about **80%** of the theoretical.

Behavior of **Mannose** Phenylhydrazone in the Presence of Acetic Acid.—A mixture of **2** g. of mannose phenylhydrazone, **10** cc. of water and 1 cc. of acetic acid did not change after standing for two days at room temperature except for a slight darkening of the liquid. It was then heated for two hours on a water-bath. Some dark resinous product was formed from which nothing could be separated. That the mother liquor contained mannose was shown by the fact that on treatment with a little phenylhydrazine it gave an almost immediate precipitate of mannose phenylhydrazone which after recrystallization melted at 200–201°. It did not depress the melting point of a sample of pure mannose phenylhydrazone melting at this temperature.

Summary

1. The reaction of glucose or fructose with an equimolecular amount of phenylhydrazine in cold dilute acetic acid gives a high yield of glucosazone,

instead of glucose phenylhydrazone as might be expected. Mannose, on the other hand, yields only the hydrazone under these conditions.

2. Glucose and fructose phenylhydrazones are converted practically quantitatively to glucosazone on standing in dilute acetic acid. Mannose phenylhydrazone is unchanged by this treatment.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

PHOTOCHEMICAL DECOMPOSITION OF LACTIC ACID

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This study of the photochemical decomposition of lactic acid is part of an investigation of the oxidation of lactic acid by oxygen in the presence of ultraviolet radiation. The investigation was undertaken as a result of a consideration of the theories of physiological chemists in regard to the oxidation of lactic acid in the body. It appeared that a study of the oxidation from a purely chemical viewpoint would be of value in connection with these theories.

Before this could be done a more thorough investigation of the decomposition of the acid, in the absence of oxygen, by ultraviolet radiation was necessary. There is a marked conflict between the results of other investigators over the decomposition of lactic acid in solution by the radiations of a quartz mercury arc. The differences found may be explained, in part, by taking into consideration the fact that some observers exposed the irradiated solution to air and some took the necessary precaution to see that no oxygen was present. Another discrepancy arose from the fact that some observers used glass containers. The wave lengths of radiation that decompose lactic acid are absorbed by glass.

Bolin[1] states that there is no decomposition of lactic acid in glass flasks. Euler's[2] investigation showed that at 70° alcohol and a gas mixture composed of 90% of carbon dioxide and 10% of hydrogen and carbon monoxide resulted. No substance was formed that reduced Pehling's solution. More recently Euler,[3] in experiments carried out both at **30** and 70°, confirms these results. He states that no reaction takes place in glass flasks. In all his experiments he finds an induction period of about two hours. This was, doubtless, the length of time necessary to produce enough carbon dioxide to saturate the solution. Euler's results were confirmed by Scharz[4] with the exception that methane was also found in small

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[1] Bolin, *Z. physik. Chem.*, **87**, 493 (1914).

[2] Euler and Lindberg, *Biochem. Z.*, *39*, 410 (1912).

[3] Euler and Ryd, *ibid.*, 51, 96 **(1913).**

[4] Scharz, *Arch. ges. Physiol.*, *170*, *650* (1918).

quantities. Neuberg,[5] in criticizing Euler's results, claims that there is no decomposition in quartz flasks when exposed to the radiation from a mercury arc. This conclusion was based on the fact that no evolution of carbon dioxide was observed and that titration of the irradiated solution showed no loss of acid. The failure to obtain carbon dioxide gas could be explained on the basis of the fact that the rather low radiation intensity used would not give enough carbon dioxide to saturate the solution. The fact that the amount of lactic acid remains unchanged is based on the assumption that no other acid is formed under the conditions of his experiment. Baudisch[6] states that no alcohol, no methane and no carbon monoxide were found, but that acetaldehyde was found in large quantities. Neuberg's and Baudisch's results differ greatly from Euler's and those of the present investigator.

Apparatus

The apparatus used in this experiment although designed for the study of the oxidation of lactic acid was fairly well adapted to measuring the decomposition. Two sources of radiation were used. One was a commercial, 220-volt, Cooper-Hewitt quartz mercury arc A operated at 3.1 amperes. This lamp had been used previously for about 500 hours. It was air-cooled by a steady blast at 22°. The other was an iron arc operated at 15 amperes from a 220-volt line. The voltage on the line was held steady by adjusting resistances at the motor generator unit. The visible and ultraviolet radiation from the mercury arc did not vary over 3% in the course of a day. The reaction tube T was placed in a tin-lined thermostat B. The thermostat had a 5 cm. by 15 cm. quartz window Q in the front and a smaller one in the back. In order to remove carbon dioxide from the solution it was found necessary to shake the tube vigorously as well as to evacuate it; otherwise as much as 6 cc. of the gas would remain in the solution. For this reason the reaction tube was mounted on a slide and could be shaken over a 6-cm. stroke at 310 r.p.m. The reaction tube itself was made by the General Electric Company from ground and polished quartz plates fused together to form a square container with internal dimensions of 1.9 X 1.9 X 10.0 cm. At one end a neck 10 cm. long and 0.4 cm. in internal diameter was fused. The tube for the removal of gases was ground into the mouth of the reaction tube and extended the length of the neck. Rubber tubing was wired over the joint; 25 cm. of heavy rubber tubing led from this tube to the 2-mm. bore glass tube from the Töpler pump. The pump delivered the gas directly to the buret of the gas analysis apparatus. Radiation from the arc passed successively through the quartz window, 3.8 cm. of distilled water, the reaction vessel, 0.5 cm. of water and out the

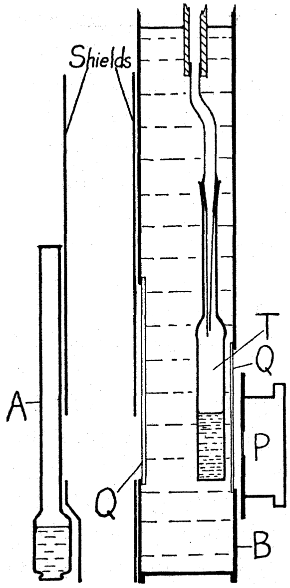

Fig. 1.

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[5] Neuberg, Biochem. Z., **13,** 303 (1908); **29,** 279 (1910); **39,** 163 (1912).

[6] Baudisch, *ibid.,* **103,** 59 (1920).

back window. The thermopile P was one made by Coblentz of the Bureau of Standards for the Vermont Agricultural Experiment Station and was loaned by them for this work. The galvanometer was used as a zero instrument, the current from the thermopile being balanced by a certain fraction of a measured current.[7] The thermopile was standardized by a Bureau of Standards standard of radiation. 0.1302×10^{-3} cal. per $cm.^2$ per min. gave an e.m.f. of 1.55×10^{-6} volts. This standardization depends somewhat on the assumption that the thin quartz window on the thermopile reflects and absorbs the same amount of radiation from the hot carbon filament of the standard of radiation as it does from the source to be measured.

Experimental Part

Absorption Measurements.—In order to determine the wave lengths absorbed, a series of photographs of the absorption spectrum was made. These were made both with the reaction tube and with a cell the thickness of which could be varied. The results showed that very little radiation of wave lengths longer than 2500 Å. was absorbed and that practically all below that value was absorbed. As most of the radiation from this arc below 2500 Å. was concentrated in five lines between 2330 Å. and 2500 Å., the average wave length of absorbed radiation was taken as 2450 Å.[8] Absorption measurements were made by comparing the amount of radiation transmitted by the reaction tube filled with water and-with a lactic acid solution. As the sides of the tube had been slightly distorted when it was fused together, care was taken to see that it was in the same position for each measurement. The arrangement for shaking permitted this without difficulty. Absorption measurements were also made with a 23-mm. tube with quartz windows fastened on by de Khotinsky cement. In this case the radiation was first run through 6.6 cm. of water to remove most of the heat radiated from the lamp. The absorption measurements were all fairly unsatisfactory as the lamp was not steady and showed variations of about 1% over short periods of time. Values were obtained ranging from 3.7 to 4.5%. Most of the measurements were between 4.1 and 4.2%. 4.15% was used as the value. The radiation intensity was measured at the back window. The ratio between this value and that at the position of the reaction cell was determined by experiment.

Lactic Acid.—The lactic acid (Kahlbaum) was prepared by rapid distillation at 5 mm. pressure. Only the constant boiling point fraction was used. After distilling, it was diluted to approximately 1 *N* and refluxed for eight hours to hydrate all lactide.[9] The normality was found to be 1.137 (by oxidation) and 1.140 (by titration with phenolphthalein).

Quantum Yield Determinations.—In the experiments described below the temperature of the thermostat was 25.00' and the gas volumes are corrected to 0° and 760 mm. The lactic acid solution was run into the reaction tube until the bottom of the meniscus was 4.5 cm. from the bottom of the tube. It was then placed in the shaking apparatus in the thermostat, The thermostat was emptied, rinsed out with distilled water and refilled with distilled water. It was found to be important to change the water every run. The tube was evacuated, with shaking between the strokes of the Töpler pump, until no more gas could be pumped out, The shutter in front of the thermostat was then opened to the extent of 4.5 cm., exposing the solution to the quartz mercury arc. A shield was placed close to the arc so that only 4.5 cm. of the tube of the arc was exposed. At the end of the exposure the arc was turned off and the gas pumped out of the solution as described above. This gas was analyzed for carbon dioxide; then oxygen

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[7] G. R. Burns, Vermont Agricultural Experiment Station Bulletin, 261 (1927).

[8] "International Critical Tables," Vol. 5.

[9] Dietzel and Krug. *Ber.*, 583, 1307 (1925).

was admitted and the mixed gases were run over a hot platinum spiral; the carbon dioxide thus formed was then determined. Typical runs are given in Table I.

TABLE I

QUANTUM YIELDS OF CARBON DIOXIDE

Duration of irradiation, hours	6	6	6
Av. radiation intensity at tube, microvolts	359.5	386.4	372.0
Surface exposed, square centimeters	8.55	8.55	8.55
Carbon dioxide produced, cc.	4.94	5.15	4.90
Decrease on ignition, cc.	0.51	0.53	0.42
Carbon dioxide produced by ignition, cc.	0.50	0.50	0.38
Moles of carbon dioxide found X 10^4	2.220	2.315	2.202
Moles of carbon dioxide calculated X 10^4	3.30	3.55	3.41
Quantum yield on carbon dioxide produced, %	67.4	65.2	64.7

Analysis of Gas.—The gases other than carbon dioxide comprised about 9% of the total volume of gas formed. These gases were investigated as follows. A 54-hour run with the reaction tube three-quarters full and exposed to the full length of the mercury arc gave 168.36 cc. of gas. This was analyzed in a special apparatus with the following results:[10] 153.10 cc. of carbon dioxide, 1.50 cc. of unsaturated compounds, 6.44 cc. of carbon monoxide, 16.99 cc. decrease on ignition with oxygen, 11.08 cc. of carbon dioxide produced by ignition. The ratio, 1.53, between the decrease on ignition and carbon dioxide produced is very close to that which would be produced by 3.67 cc. of methane and 3.67 of ethane. If this mixture of gases had been analyzed by the method customarily used in this investigation, a decrease on ignition of 23.20 cc., and the formation of 20.52 cc. of carbon dioxide would have been found. This ratio is roughly the same as that usually obtained (Table I).

When the iron arc was substituted for the mercury the results in Table II are typical of those obtained.

TABLE II

DECOMPOSITION BY IRON ARC

Carbon dioxide in two hours, cc.	1.40	1.31
Decrease on ignition, cc.	0.21	0.23
Carbon dioxide produced by ignition, cc.	.14	.13

This shows that the higher percentage of short wave lengths from the iron arc produces a different type of decomposition from that produced by the mercury arc. It shows also that the mixture of gases produced above will change in composition with increasing age of the mercury arc. For these reasons, and because the length of time necessary to produce samples of this gas was so great, the experiment was not repeated.

Determination of Ethyl Alcohol.—Ethyl alcohol was found in substantial quantities. The amount was determined by the Bourcart–Kuriloff method.[11] This consists of oxidizing the alcohol to acetic acid by potassium dichromate and sulfuric acid at 100° in a sealed tube, treating the excess dichromate with potassium iodide and sulfuric acid and titrating the iodine by freshly standardized sodium thiosulfate. The applicability of the method to the present type of analysis was as follows. A solution containing 0.020 g. of ethyl alcohol was found to be equal to 8.75 cc. of 0.200 N dichromate: calcd. 8.69 cc. This was within the error in weighing out the 2 g. of alcohol from which the alcohol

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[10] Analyzed with the aid of Dr. Huffman of this Laboratory, who has had much experience with this type of analysis.

[11] Poznanski, THIS JOURNAL, 50, 981 (1928).

solution was prepared. It was found that oxidizable material equivalent to 0.33 cc. of 0.200 N dichromate would distil from the unirradiated lactic solution. This was due to impurities, as the second fraction distilling showed no reaction with dichromate. That all of the alcohol would distil was shown by putting 0.020 g. of alcohol into 16.2 cc. of lactic acid solution and distilling it according to the procedure below: dichromate used, 9.10 cc.; calcd. 0 33 cc. plus 8 75 cc. = 9.08 cc.

The 16.2 cc. of irradiated lactic acid solution was washed into a 100-cc. flask and 8.0 cc. of 20% sodium hydroxide added. Ten cc. was then distilled off through a short air-cooled reflux condenser in about thirty minutes. Typical determinations are given in Table III.

TABLE III

RATIO OF ALCOHOL TO CARBON DIOXIDE

Carbon dioxide produced in seven hours, cc.	20.10	21.70
0.200 N $K_2Cr_2O_7$ used, cc.	21.63	23.64
Moles of carbon dioxide produced X 10^4	9.04	9.74
Moles of alcohol found $\times 10^4$	10.65	11.67
Carbon dioxide/alcohol ratio	1:1.18	1:1.20

Test for Acetaldehyde.—Although no aldehyde could be detected after any run, either in the solution or in the gases pumped out, one quantitative test for it was made. The Schiff's reagent was prepared by Alyea and Bäckström's method.[12] A lactic acid solution was irradiated, after all air had carefully been removed, for six and one-half hours with an intensity great enough to produce 21 cc. of carbon dioxide. The apparatus was so arranged that substances distilling from the solution were condensed and held in an unirradiated trap. The liquid from the trap was then returned to the reaction tube, the tube packed in ice and left for an hour. At the end of this period it was opened, the contents made up to a volume of 25 cc. and 10 cc. of Schiff's reagent added. For purposes of comparison a 0.0006 M aldehyde solution and a blank were prepared. To 25 cc. of the former (1.5 X 10^{-5} mole of aldehyde) 10 cc. of Schiff's reagent were added. The latter consisted of 25 cc. of distilled water plus 10 cc. of Schiff's reagent. The unknown solution developed no color and when compared in a colorimeter was identical with the blank. The 0.0006 M aldehyde solution developed a strong pink color.

The amount of carbon monoxide produced in this run must have been about 0.84 cc. If some of the lactic acid had decomposed into carbon monoxide and acetaldehyde this would correspond to a production of 4.0 X 10^{-5} moles of the aldehyde. It would seem that this amount of aldehyde would give a test even though most of it were destroyed by the action of the radiation.[13]

Discussion of Results

As the decomposition of lactic acid is approximately a quantum reaction, it was not possible to use monochromatic illumination and obtain appreciable quantities of the products. The radiation absorbed comprised so small a portion of the spectrum of the mercury arc that the error from this source in determining the quantum yield was not over 2%. The fact that several wave lengths were absorbed meant that several decomposition reactions were taking place concurrently. Exactly one hundred runs were

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[12] Alyea and Bäckström, THIS JOURNAL, 51, 97 (1929).

[13] Ellis and Wells, "The Chemical Action of Ultra-Violet Rays," 1925, p. 155.

made, and, in each, as many products were investigated as could be tested in the same experiment. Successive runs only are used as examples in this paper.

Lactic acid, $CH_3CHOHCOOH$, might break up into a carbon dioxide and alcohol. It was found that this was the main decomposition, as 90.9% of the gas given off was carbon dioxide. Vigorous shaking of the reaction tube in addition to evacuation was found to be necessary to remove all of the carbon dioxide from the solution. The neglect of these precautions accounts, in part, for the erratic results of previous investigators. The amount of carbon dioxide found corresponded to a quantum yield of about 0.65 molecule per quantum. As the amount of radiation absorbed could not be satisfactorily determined, the error from this source may be as much as 10%. The other factors necessary to determine the quantum yield were measured to a much higher degree of accuracy.

The amount of alcohol found in the solution was 19% in excess of the quantity required by the assumption that the lactic acid decomposed into equal amounts of alcohol and carbon dioxide. The reason for this discrepancy has not yet been determined. In order to avoid removing alcohol vapor the gases were not as completely removed from the solution in cases where the alcohol content was to be determined as in other instances. The amount of carbon dioxide left in solution was very much less than the amount required to account for this discrepancy. As the alcohol was determined by oxidation of the distillate from a strongly alkaline solution of the reaction mixture, there might have been present other substances which were also oxidized but, as there was no aldehyde, it is difficult to imagine an impurity that could have been present. The method of determining alcohol was accurate to 0.5%. The quantum yield based on the amount of alcohol produced is about 0.77 molecule per quantum.

It is interesting to consider the reactions that took place other than the main decomposition into alcohol and carbon dioxide. The additional substances found in the gas were: (by volume) unsaturated compound (probably ethylene), 0.89%; carbon monoxide, 3.82%; methane (calculated), 2.18%; ethane (calculated), 2.18%. If one molecule of lactic acid is decomposed into ethylene, carbon dioxide would be produced in equal amounts. This would mean that 0.98% of the carbon dioxide came from this decomposition. If methane is one of the products formed, the other might be two molecules of carbon monoxide. The carbon monoxide found was 87% of that required by this decomposition. Carbon monoxide might also be formed by a decomposition giving acetaldehyde as the other product. As a quantity of the aldehyde much less than that required by this reaction could have been detected it was assumed that this decomposition did not take place. One molecule of the acid might give ethane and hydrogen peroxide or its decomposition products. No hydrogen peroxide was found. Oxygen, in the few cases in which it was found, was accompanied by nitrogen and was assumed to have been the result of air leaking into the apparatus. Ethane might have been formed by the decomposition of two molecules of the acid, yielding ethylene glycol as the other product. No attempt was made to find this trace of ethylene glycol as the author's previous experience with this compound did not Lead to the belief that it could be detected.

Summary

1. Lactic acid in water solution is decomposed by radiations of wave lengths shorter than 2500 Å. The chief products of decomposition by radiations from a quartz mercury arc are alcohol and carbon dioxide. Carbon monoxide, saturated hydrocarbons and unsaturated hydrocarbons form about 9% of the gaseous products.

2. Aldehyde, if produced, is present in quantities less than 1% of the total decomposition products.

3. The ratio between the energy absorbed and the carbon dioxide produced corresponds to a quantum yield of approximately 0.65.

4. More ethyl alcohol is produced than is required by the assumption that lactic acid decomposes into equal amounts of alcohol and carbon dioxide.

NEW HAVEN, CONNECTICUT

NEW BOOKS

Das Buch der grossen Chemiker. (The Book of the Great Chemists.) Edited by Dr. GÜNTHER BUGGE with the cooperation of special scholars. Vol. I. From Zosimos to Schonbein. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1929. xii + 496 pp. Illustrated. 16 X 24 cm. Price, unbound, M. 21; bound, M. 24.

This is a book for the chemist's leisure. The publisher's advertisement says that biographical essays in the history of chemistry have not before been published in the German language. The various chapters have been written by scholars who are well known for their researches in the history of chemistry and generally include the latest knowledge on the subjects with which they deal. The first volume brings the account nearly up to the middle of the nineteenth century, and contains chapters on Zosimos (Ruska), Jabir (Ruska), Albertus Magnus (Strunz), Roger Bacon (Strunz), Raymund Lull (Strunz), pseudo-Geber (Ruska), Biringuccio (Johannsen), Paracelsus (Strunz), Agricola (Darmstaedter), Libavius (Darmstaedter), pseudo-Basil Valentine (Fritz), Van Helmont (Strunz), Glauber (Walden), Boyle (Farber), Stahl (Koch), Boerhaave (Speter), Goeffroy the Elder (Speter), Marggraf (Speter), Black (Speter), Cavendish (Lockemann), Priestley (Lockemann), Scheele (Lockemann), Leblanc (Bloch), Lavoisier

(Speter), Klaproth (Bugge), Berthollet (Farber), Proust (Farber), Fourcroy and Vauquelin (Bloch), Davy (Ostwald), Faraday (Ostwald), Berzelius (Soderbaum), Mitscherlich (Bugge) and Schonbein (Farber).

It is apparent that we cannot charge Dr. Bugge, as Colson charged Ladenburg, with overemphasizing the part which Germans have played in the development of chemistry. Indeed we think that another German ought to have been included—Kunckel, who discovered fulminate and phosphorus, and manufactured ruby glass, whose writings first turned Scheele toward chemistry, a man who early developed the applications of chemistry, not alchemy, to the production of *thalers*. His school is numerous in the twentieth century. And there ought certainly to have been a chapter on Lomonosov.

The illustrations are excellent, old prints, pictures of apparatus and portraits which have been chosen with care. A reproduction of an autograph recipe of Paracelsus is very convincing. The book is well bound, well indexed, and well printed in a modernistic manner with paragraphs commencing at the margin. The book can be recommended to chemists in general and to students who wish to improve their chemistry or their knowledge of literary German. Each chapter is an adventure. The book will surely have a wide circulation.

TENNEY L. DAVIS

The Corrosion of Metals. Part I. General Theory. BY PROFESSOR WILH. PALMAER, D.Sc. Ingeniorsvetenskapsakademiens Handlingar Nr 93. Svenska Bokhandelscentralen A.-B., Stockholm, Sweden, 1929. 347 pp. 101 figs. 5 plates. 16.5 × 24 cm.

This Memoir (in English) of the Royal Swedish Institute for Scientific-Industrial Research of Stockholm gives an extended account of the investigations that Professor Wilh. Palmaer and his associates have been conducting since 1920 on the corrosion of metals. Two brief preliminary summaries of these investigations have already been published, one in Sweden and one in Germany.

The author first gives a thorough discussion of earlier theories of the solution of metals in aqueous solution. The *Theory of Local Galvanic Elements* is discussed with particular thoroughness. Several experimental investigations are then presented in detail, as follows: (a) the Velocity of Solution of Aluminum in Acids; (b) the Voltage Required to Deposit Hydrogen on Graphite; (c) the Velocity of Solution of Iron in Acids; and finally (d) the Velocity of Solution of Calcium Carbonate in Acids.

The bearing of these results and of those obtained by others in similar researches on the three main theories of this phenomenon are then discussed at length, the conclusion being that the primary factor in the solution of metals in acids is the activity of local galvanic elements. Various consequences of this conclusion are then examined and certain catalytic phenomena are explained.

Part II is to deal with special researches on the solution of metals; Part III with the special theory of the corrosion of iron.

This comprehensive and exhaustive study of a scientific and practical problem of the first importance will be of great interest to the many chemists and engineers who are concerned with it.

ARTHUR B. LAMB

The Theory and Technique of Quantitative Analysis. BY MARIE FARNSWORTH, Ph.D., Instructor in Chemistry, Washington Square College, New York University. John Wiley and Sons, Inc., New York, 1928. vii + 154 pp. 34 figs. 15 X 23.5 **cm. Price, $2.50.**

This little book differs from other books on this subject in that its purpose is not to describe definite procedures but to classify and generalize the operations and to apply the theory of quantitative analysis. Most courses in this subject lay too much stress on the ability of the student to obtain results merely by following a definite set of directions and too little on a thorough discussion of the theory involved. In the laboratory the student is too often left to acquire the technique as best he can, and although it can best be taught by demonstration, this book will at least acquaint him with the tools of the analyst and his manner of working.

It is obvious that this book is mainly the work of Dr. Wendt although his name does not appear as co-author.

Chapters are devoted to the balance and its use, to reagents, laboratory ware, preparation of samples, precipitation and filtration, as well as to the various types of volumetric reactions. The nephelometer is briefly described but unfortunately nothing is said about colorimetric methods, which are more commonly used than nephelometric. Chapters on electrolytic processes and electrometric titrations complete the book.

Inasmuch as many students in quantitative analysis have not yet studied physical chemistry, a book of this type will be of great assistance. In presenting the theory as simply as possible, the author has not made much mention of the many cases to which the simple theory will not apply. For example, the solubility product principle is not as generally applicable as might seem from the chapter in which this subject is discussed, owing to the disturbing effects of hydrolysis, complex formation and presence of other salts.

Attention might be called to a few errors and omissions which can readily be corrected in a future edition. The reviewer cannot agree with the optimistic statement on page **32** that sillimanite ware "rarely breaks when dropped from the laboratory table to the floor." On page 140 it is recommended to remove platinum black from a hydrogen electrode previous to replatinizing by means of sandpaper; it is difficult to imagine anyone doing it that way. The chapter on filtration should include descriptions of sintered glass and porous porcelain filtering crucibles. On page 97 in the list of primary acidimetric standards, potassium acid phthalate is not included, although it answers every requirement and is issued by the Bureau of Standards. The use of the ball mill in grinding samples and the electric muffle for ignitions should be mentioned.

This book can be heartily recommended to all students in quantitative analysis.

H. H. WILLARD

Die anisotropen Flüssigkeiten. (Anisotropic Liquids (Liquid Crystals).) BY C. W. OSEEN, Professor at the University of Upsala. Gebrüder Borntraeger, W 35 Schöneberger Ufer 12 a, Berlin, Germany. 1929. iii + 87 pp. 5 figs. 16.5 × 25.5 cm. Price, unbound, RM. 6.80.

Here at last is the long desired monograph, the only balanced and unbiased account of the highly important yet little known field of liquid crystals. Lehmann's discovery and exploration of this truly remarkable subject earned for him much obloquy and sharp recrimination from many sides, continued throughout his lifetime. The subject is still regarded in most quarters as a somewhat doubtful scientific curiosity. It will be news to most men of science of the present time that Vorlander has prepared 2000 different substances in one or more of the liquid crystalline or anisotropic liquid states. It will be news to almost every chemist that perfectly stable material in this condition is being manufactured and sold in the form of soap solutions on the scale of thousands of tons. Every soap is capable of forming two kinds of liquid crystal, existing over a wide range of temperature and concentration.

The subject of liquid crystals has suffered from the fact that most exemplars of this state are complicated organic compounds easily decomposed by excessive heating and yet exhibiting these states only over comparatively narrow ranges of elevated temperature, usually observed only in microscopes provided with heating stages and water-cooled objectives. These liquids are doubly refracting, like crystals, and often spontaneously assume highly characteristic and hitherto totally unexplained shapes, as, for example, the double cone of an ammonium oleate droplet. The adequate elucidation of this group of states of matter, which cannot be called gaseous, liquid or crystalline, is obviously *a* problem of first class importance.

Oseen, who in his own papers has developed a highly mathematical treatment, has avoided this almost completely in his admirable review of the subject. He has brought together *a* most interesting account of the quantitative studies of various phenomena such as the dependence of electrical and other physical properties on direction in a liquid crystalline phase. It is very interesting to note that none of the English speaking countries have contributed anything worthy of mention to this subject. It has been developed exclusively by Germans, French, Dutch and Swedes. Oseen's monograph is held together by constantly referring the phenomena and measurements described to the touchstone of a comparison between the general theory of Oseen and its somewhat primitive rival, the dipole theory of Riecke (1905) adopted by Vorlander (1910) and given quantitative form by M. Born and F. Grandjean in 1916 and 1917.

JAMBS W. MCBAIN

Elements of Physical Chemistry. BY JAMES M. BELL, Head of the Department of Chemistry, University of North Carolina, and PAUL M. GROSS, Head of the Department of Chemistry, Duke University. Longmans, Green and Co., 55 Fifth Avenue, New York, 1929. xiii + 466 pp. 88 figs. 13.5 X 21 cm. Price, $3.75.

The authors describe this volume as prepared with the college student in mind who has had a course in "General Chemistry, Analytical Chemistry and Organic Chemistry, and who has had a course in General Physics and preferably in the Calculus." In the text the kinetic theory, behavior of solutions, crystal structure, equilibrium and phase rule are among those topics which are particularly emphasized. An interesting chapter on Polar Properties of Solutions is included. The derivation of equations throughout the text is very clear cut. Descriptive matter is not included in large measure, the topics of atomic structure and colloid chemistry being described rather briefly and radioactivity being omitted entirely. Each chapter is followed by ten or a dozen problems with answers at the end of the book.

The volume is also a laboratory manual, giving at the conclusion of fourteen of the chapters a laboratory experiment illustrative of the foregoing principles. No special apparatus is required for most of these experiments.

The text is well illustrated with diagrams which are particularly legible and the experiments by large clear drawings.

HENRY E. BENT

Colloid Chemistry. BY THE SVEDBERG, Professor of Physical Chemistry, University of Upsala. Second edition, revised and enlarged in collaboration with ARNE TISELIUS, Research Assistant in Physical Chemistry, University of Upsala. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc, 419 Fourth Ave., New York, 1928. 302 pp. 167 figs. 15.5 × 23.5 cm. Price, $5.50.

The special lectures on Colloids given by Professor Svedberg and the research which he organized on his visit to the University of Wisconsin during the spring and summer of 1923 not only gave an immense impetus to the study of Colloids in this country but culminated in the brilliant development of the author's experimental methods on the grand scale, providing a new and invaluable method for the investigation of some of the most obstinate problems of chemical and biological science. The prompt publication of Svedberg's lectures as an outstanding volume of the American Chemical Society's series of monographs did much to fructify the study of some of the more quantitative aspects of colloid science.

Now after five years, during which the author has become a Nobel Prizeman, we have a new and enlarged edition in which the remarkable invention of the ultracentrifuge is described and some of its many varied fields of application in general science are illustrated by actual results. The quantitative information that will come from the use of this unfortunately very costly apparatus is bound to become as distinctive and important as, for example, the study of everyday materials by X-rays. The exposition of these two methods constitutes the most important addition in the present edition, although the whole book has been thoroughly revised.

This is one of the few indispensable works of colloid science. Nevertheless, one is bound to point out that the title is somewhat of a misnomer, since there is comparatively little chemistry in the book. The strength of the treatment lies in its one-sidedness, in the full presentation of the study of colloids in relation to kinetic theory, a field in which the author has played so prominent a part.

JAMES W. MCBAIN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PRECIPITATED SELENIUM DIOXIDE[1]

BY G. F. HOFFMANN AND VICTOR LENHER

RECEIVED DECEMBER 13, 1928 PUBLISHED NOVEMBER 8, 1929

Many unsuccessful attempts have been made to prepare the hypothetical trioxide of selenium analogous to the trioxides of sulfur and tellurium. Worsley and Baker[2] were the first investigators to report the preparation and properties of this compound. In brief, their method of preparation consisted of the oxidation of selenium dissolved in vacuum distilled selenium oxychloride by ozone. Following the publication of their researches, two former students of V. Lenher attempted the preparation of selenium trioxide but failed to obtain products which corresponded in selenium content to the trioxide and which responded to available oxygen tests for hexavalent selenium. Recently Julius Meyer and Anton Pawletta[3] reported their failure to obtain the trioxide by the above method and concluded that the oxidation product was selenium dioxide containing selenium monochloride as an impurity.

The following investigation was begun in 1925 and completed in January 1927, previous to the publication of Meyer and Pawletta. The data given not only establish the identity of oxidation products obtained, but prove the non-existence of selenium trioxide in products prepared according to Worsley and Baker's method.

Materials

Selenium.—Pure, resublimed selenium dioxide was dissolved in 10% hydrochloric acid and selenium subsequently precipitated by the addition of sulfur dioxide. Precipitated selenium was washed by decantation until free from acid, then boiled in distilled water, filtered and finally fused and cast in the form of sticks.

Selenium Oxychloride.—Lenher's[4] method of preparation was used. The oxychloride was fractionally distilled several times at 17 mm. pressure in a moisture-free

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[1] Extract from a dissertation submitted by G. F. Hoffmann in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

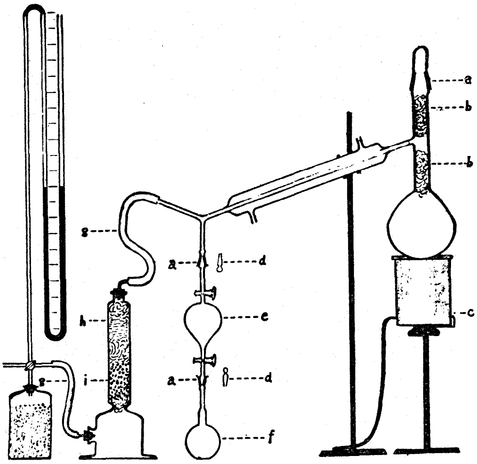
[2] Worsley and Baker, J. *Chem. Soc.*, 2870 (1923).

[3] Meyer and Pawletta, *Ber.*, 60, 985 (1927).

[4] Lenher and Kao, THIS JOURNAL, 42, 2498 (1920).

system (Fig. 1). Extremely dry selenium oxychloride was obtained by fractional distillation at reduced pressure from resublimed phosphorus pentoxide. The purity of the distillate was confirmed by freezing point determinations and the molybdate test for phosphate. Absorption of moisture by selenium oxychloride during transference from the still receiver was avoided by draining the distillate directly into reaction flasks through ground-glass joints.

Ozone.—Oxygen produced by the fractional distillation of liquid air was employed. Precautions to insure the absence of impurities such as hydrogen, carbon dioxide and water were taken, as shown in Fig. 2. Concentrations of ozone varying between 2 and 6% were produced in a triple cell ozonizer.



a,a,a, Ground glass joints; b,b, glass wool; c, electric heater; d,d, ground glass stopper; e, receiver bulb; f, fractionating bulb; g,g, suction tubing; h, phosphorus pentoxide; i, calcium chloride.

Fig. 1.—Selenium oxychloride distilling apparatus.

Carbon Tetrachloride.—Dry carbon tetrachloride was prepared by double distillation from phosphorus pentoxide immediately before use.

Analytical Methods

Selenium.—Selenium was determined giavimetrically according to the method of Lenher and Kao[5] It was precipitated in the presence of 15% hydrochloric acid by sulfur dioxide and hydroxylamine hydrochloride. Precipitation was allowed to take place slowly at room temperature. The supernatant liquid was decanted through a tared Gooch crucible and the precipitate remaining in the beaker was converted to gray crystalline selenium in boiling water. It was then brought on the same crucible, washed with water and alcohol, dried at 105° and weighed.

Available Oxygen.—Selenic acid and all selenates liberate free chlorine from hydrochloric acid solutions.[6] According to Worsley and Baker the product of ozone oxidation of selenium in selenium oxychloride reacts with water to give selenic acid; hence a water solution of the product should liberate chlorine from a hydrochloric acid solution.

Available oxygen was accurately determined by gently boiling a 10% hydrochloric acid solution containing a hexavalent selenium compound and conducting the liberated chlorine into a solution of potassium iodide slightly acidic with sulfuric acid. Iodine was titrated with $N/10$ sodium thiosulfate solution. The distillation of chlorine into iodide solution was aided by a slow current of carbon dioxide. This method is in common use for the determination of hexavalent selenium.

Chlorine.—Chlorine was determined in the presence of selenium by precipitation as silver chloride from solutions containing approximately 10% nitric acid and an excess of silver nitrate. The accuracy of such analyses was established hy numerous trial analyses of solutions which were prepared to contain known amounts of selenious or selenic acid, nitric acid and chloride.

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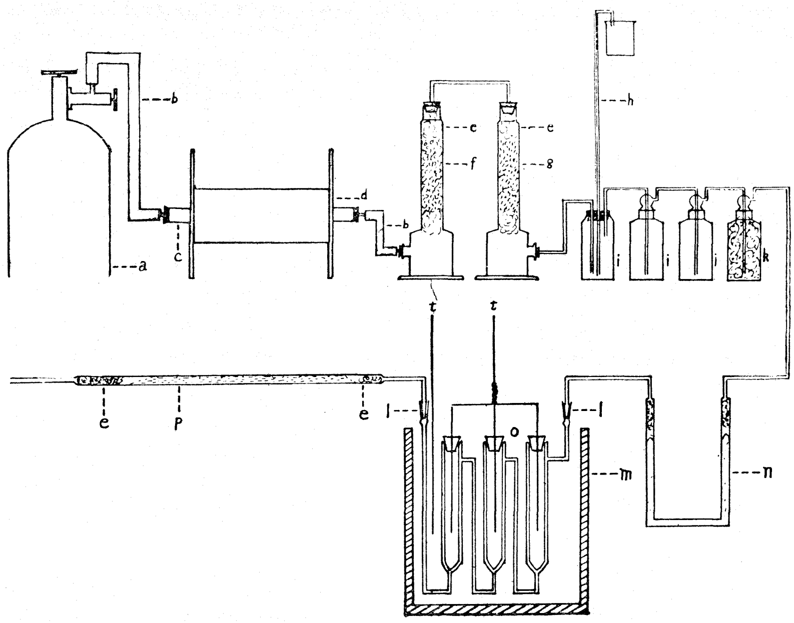
[5] Lenher and Kao, This Journal, 47, 769 (1925).

[6] Petterson, *Fres. Zeit.*, 12, *287* (1873).

Water.—The water content of precipitated selenium dioxide was determined according to the method developed by A. Julien[7] for sublimed selenium dioxide. Samples were manipulated in a box desiccator as a precaution against absorption of moisture from the air in the laboratory.



a, Oxygen tank; b,b, suction tubing; c, porcelain tube, filled with copper oxide; d, electric furnace; e,e,e, glass wool; f, soda lime; g, calcium chloride; h, safety tube; i,i,i, concentrated sulfuric acid; k, glass wool and phosphorus pentoxide; l,l, ground glass joints; m, cooling bath; n, phosphorus pentoxide; o, triple cell ozonizer; p, pure phosphorus pentoxide; t,t, high tension leads.

Fig. 2.—Preparation of pure ozone.

Experimental Details

A reaction flask similar to that described by Worsley and Baker was used in the preparation of the first products. One modification of their apparatus was adopted. It consisted of an additional tube filled with resublimed phosphorus pentoxide inserted between the ozonizer and the reaction flask. This additional drying precaution was taken following the observation that water was formed in the ozonizer when hydrogen was not completely removed from the oxygen by reaction with hot copper oxide. The low selenium results of Worsley and Baker might be traced to this point since their ozonizer was connected directly with the reaction flask, allowing any water formed to be absorbed by the product.

The time required for a precipitate to appear on passing ozone through the selenium oxychloride solution of selenium varied between twenty and seventy hours. A white sublimate was formed on the walls of the reaction flask and gas outlet tube. Precipitates were brought on dry asbestos filters and thoroughly washed with dry carbon tetrachloride in the absence of moist air. Dry air was drawn through the washed precipi-

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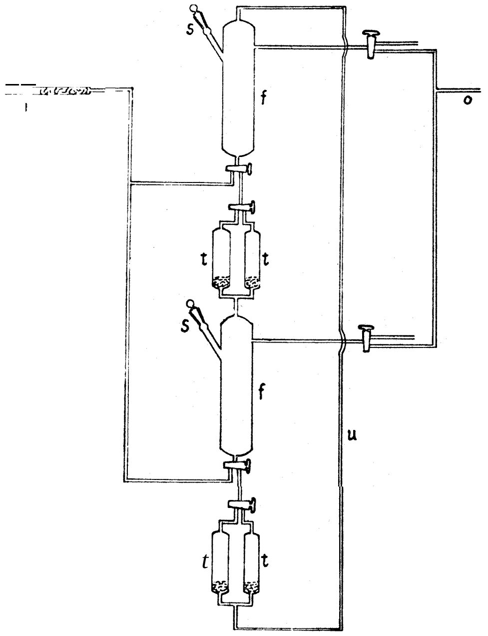
[7] Julien, This Journal, 47, 1799 (1925).

tates to remove the carbon tetrachloride. The use of absolute ether for washing purposes was abandoned following the observation that the color of the product was changed from white to yellow or pink when in contact with pure ether. Upon mixing the oxychloride filtrate of a product with dry carbon tetrachloride a white precipitate was formed. This precipitate resembled the original product in appearance and composition.

Analytical results of the products of ozone oxidation of selenium oxychloride solutions are summarized in Table I. For preparations I–VII, inclusive, vacuum distilled selenium oxychloride was used as the solvent medium. Due to the variable selenium content of the first products, analyses for water and chlorine were included for all subsequent products. After the presence of water in Products V, VI and VII was definitely established, it was concluded that vacuum distilled selenium oxychloride was not dry in spite of numerous fractional distillations. In an attempt to prepare dry products, an apparatus consisting of two reaction flasks connected in tandem but separated by filtering tubes was constructed. A series of products was obtained in this apparatus by using the same solvent. In Table I the third and fourth precipitates of Preparation VIII and the second and third of Preparation IX represent products prepared in such an apparatus. Although a few drops of water were added to the solution of selenium in selenium oxychloride before starting Preparation IX, Precipitate 2 was found to contain only 0.23% of water. The major portion of the water presumably was removed from the solution by the first precipitate.



f,f, Reaction flasks; i, ozone–oxygen inlet tube; o, gas outlet; s,s, ground glass stoppers; t,t, filters; u, tube used for returning filtrate to upper reaction flask by means of gas pressure in f and suction applied at the upper three-way cock on the gas outlet tube.

Fig. 3.

It was found practically impossible to wash products entirely free from $SeOCl_2$. Several products were found to contain chloride after having been washed continuously with dry carbon tetrachloride for one week. It appeared perfectly logical to consider the chlorine in the product to be present as selenium oxychloride. It is not likely that chlorine should be present as the monochloride, as supposed by Meyer and Pawletta, because selenium monochloride is readily oxidized by ozone, as is evident from the change in color of its solutions during contact with ozone. The presence of appreciable amounts of monochloride in the solution or in the product would impart a distinct reddish color to them.

Products X, XI and XII were prepared from oxychloride fractionally distilled from phosphorus pentoxide. Product XII was prepared in a different type of reaction flask shown in Fig. 4. Manipulation was greatly simplified in that the product was precipitated, washed, dried and weighed in the same container without coming in contact with moist air.

TABLE I

ANALYTICAL RESULTS

Preparation	Selenium, %	Available O_2, %	Chlorine, %	Water, %	SeO_2, %	$SeOCl_2$, %	Total, %
I	66.30	0.0					
	66.66	.0	..	..	...	...	...
II	70.42	.0	..	..	...	...	...
III	64.15	.0	..	..	...	...	...
	63.86	.0	..	..	...	...	...
IV	63.64	.0	..	..	...	...	...
V	...	..	..	0.66	...	...	...
	...	..	..	.95	...	...	...
VI	68.34	..	4.52	.96	88.80	10.59	100.35
	68.28	..	4.57	.97	88.78	10.71	100.45
VII	70.07	.0	1.56	.46	95.80	3.65	99.91
	70.19	..	1.59	..	96.04	3.72	100.22
VIII	70.88	..	0.20	.00	99.33	0.67	100.00
(3d Precip.)	71.06	..	.30	.00	99.50	.45	99.95
VIII	71.07	..	.09	.00	99.72	.16	99.98
(4th Precip.)	71.07	..	.08	.00	99.70	.18	99.98
IX	...	..	..	..	...	...	...
(2d Precip.)	70.80	..	Trace	.23	99.41	Trace	99.67
	70.97	..	Trace	.26	99.69	Trace	99.92
IX	...	..	..	..	...	...	...
(3d Precip.)	...	..	..	.00	...	...	...
X	66.47	.0	8.46	.00	80.05	17.49	97.54
	66.26	.0	8.41	.03	79.87	17.39	97.29
XI	70.52	..	0.94	.00	97.52	2.24	99.76
	70.51	..	.00	..	...	...	...
XII	69.04	.0	4.46	.00	...	...	...
	69.05	..	4.45	..	...	...	...
	68.97	..	..	..	...	...	...
	69.00	..	..	..	...	...	...

Analytical results of precipitates formed by mixing filtrates of the products with dry carbon tetrachloride are given in Table II.

The original filtrates of several products also were analyzed. Samples were weighed in tightly stoppered weighing bottles and then slowly hy-

TABLE II

ANALYTICAL RESULTS

Precip. from filtrate of product no.	Selenium, %	Chlorine, %	Water, %	SeO_2, %	$SeOCl_2$, %	Total, %
IV	70.81	..	0.31	99.63	..	99.93
	70.99	..	.37	99.67	..	100.04
VI	70.11	1.45	.00	96.20	3.40	99.60
	69.95	1.45	.00	96.00	3.40	99.40

drolyzed under water. Aliquots of the resulting solutions were analyzed for selenium and chlorine content. Results given in Table III indicate the composition of the selenium–selenium oxychloride solutions after reaction with dry ozone.

TABLE III

COMPOSITION OF FILTRATE

Sample no.	Selenium, %	Chlorine, %	SeO_2, %	$SeOCl_2$, %	Total, %
1	47.91	42.09	1.13	98.59	99.72
2	48.18	42.02	1.76	98.41	100.17
3	47.79	42.43	0.52	99.39	99.91
4	47.94	42.42	0.75	99.38	100.13
5	47.86	42.38	0.65	99.39	100.04
6	48.05	42.42	1.01	99.27	100.28

The above results and the general properties of the filtrates indicate the solvent, $SeOCl_2$, to be unchanged apparently by ozone during the oxidation of the dissolved selenium. Pure dry selenium oxychloride, however, was found to react with dry ozone when the latter was passed through a porous glass plate serving as a support for the liquid (see Fig. 4). The ozone–oxygen mixture passed through the solvent as thousands of tiny bubbles, thereby exposing an enormous surface of the liquid to the powerful oxidant. The oxidation product of $SeOCl_2$ was similar in every respect to the products obtained from $Se–SeOCl_2$ solutions.

Some Properties of Precipitated Selenium Dioxide.—Exposed to the air of the laboratory this substance rapidly absorbs water until its water content approaches 14% of the total weight of the sample; then the absorption of water practically stops. Although only approximate, this result corresponds to the water content of selenious acid.

The vapor pressure of the precipitated dioxide when moistened with water was observed to be lower than that of water alone at the same temperature; therefore, it is unlikely that oxygen was evolved when the products were dissolved in water.

Molecular Weight in Selenium Oxychloride.—A freezing point constant for selenium oxychloride was determined experimentally with solutions of ignited potassium chloride and barium chloride. An average of six determinations gave a value of 26. The molecular weights of the precipitated dioxide and the sublimed dioxide were then determined and found to be approximately three times 111.2, the calculated molecular weight of selenium dioxide. Absorption of moisture by selenium oxychloride solutions during determination of freezing points was avoided.

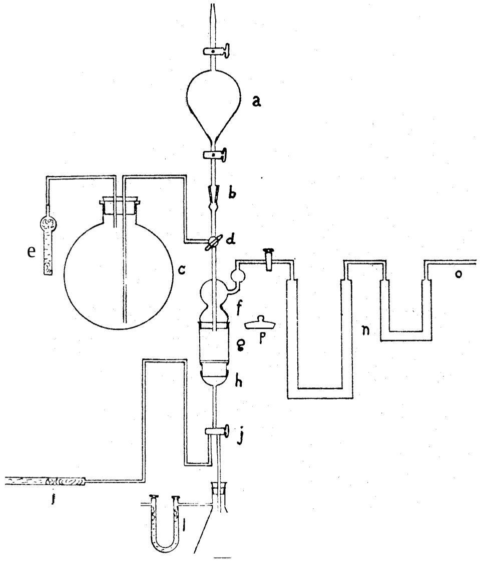
TABLE IV

RESULTS OF MOLECULAR WEIGHT DETERMINATIONS

Drop in f. p., °C.	Grams of pptd. SeO_2/1000 g. $SeOCl_2$	Mol. wt., calcd.	Drop in f. p., °C.	Grams of sublimed SeO_2/1000 g. $SeOCl_2$	Mol. wt., calcd.
0.264	3.4285	338	0.252	3.221	334
.259	3.2717	328	.239	3.078	333
.236	3.000	332	.236	2.947	325
.233	3.000	336	.227	2.886	331
.205	2.571	327	.209	2.613	325
.195	2.400	326	.184	2.347	330
.186	2.361	332	.180	2.289	331

Density of Precipitated Selenium Dioxide.—The density of precipitated selenium dioxide was determined in benzene at 20°. Two separate determinations gave 3.590 and 3.595 as the density of the product. Worsley and Baker reported 3.6 as the density of their product; therefore there can be little doubt concerning the similarity of their product and that of the authors.

A sample of precipitated selenium dioxide was exposed to moist air until a calculated amount of water was absorbed, corresponding to the water content of selenious acid. A subsequent water analysis gave 13.87% of water as compared to 13.92% of water in selenious acid. A density determination of the same hydrated oxide gave a value of 2.982 at 20°. The true density of selenious acid is d_4^{15} 3.004. Hence, within the limits of experimental error, the density of hydrated precipitated dioxide of selenium is identical with that of ordinary selenious acid.



a, Receiver of oxychloride still; b, ground-glass joint; c, 4-liter flask for washing liquid; d, 3-way stopcock; e, drying tube; f, top of Drechsel bottie; g, Jena glass crucible with waled-in sintered glass plate; h, Gooch funnel; i, oxygen ozone delivery tube; j, 3-way stopcock; 1, drying tube; m, filter flask; n, sulfuric acid traps; o, gas outlet; p, stopper for Jena glass Gooch crucible.

Fig. 4.

That the different densities of

precipitated and sublimed selenium dioxide indicate merely a difference in physical state and not in composition, is shown definitely by analyses.

"Chloroselenic Acid."—Worsley and Baker reported their selenium oxide product to absorb hydrochloric acid gas, forming chloroselenic acid, a fuming straw-colored liquid. The density of this liquid was found by them to be 2.26. The density of selenium hydroxychloride (a fuming straw-colored liquid) is 2.24 at 25°.[8]

Several samples of this substance were prepared by the authors from the precipitated selenium oxide. The resulting straw-colored liquids varied in composition and density, depending on the temperature and the time allowed for absorption. This is a characteristic property of selenium hydroxychloride. Upon plotting chlorine percentages against densities of respective samples, it was found that a straight line drawn through the plotted points passed through a point representing the density and calculated chlorine content of $SeO_2 2HCl$.

Summary

1. Attempts to prepare selenium trioxide by the method of Worsley and Baker failed.

2. The product of ozone oxidation of $Se-SeOCl_2$ solution was identified by analyses as precipitated selenium dioxide.

3. The density of precipitated selenium dioxide was found to be appreciably lower than that of the sublimed dioxide.

4. Precipitated selenium dioxide absorbs moisture rapidly to form selenious acid.

5. The molecular weights of precipitated and sublimed SeO_2 dissolved in $SeOCl_2$ were found to be identical.

6. The product of ozone oxidation of $Se-SeOCl_2$ solutions absorbs dry hydrogen chloride gas to form a fuming, straw-colored liquid similar in composition and density to selenium hydroxychloride and not chloroselenie acid.

MADISON, WISCONSIN

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[8] Muehlberger and Lenher, THIS JOURNAL, 47, 1842 (1925).

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

THE REPULSION OF ATOMIC KERNELS AS A FACTOR IN ORGANIC REARRANGEMENTS

BY WENDELL M. LATIMER

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Although the repulsion of the atomic kernels is an obvious factor[1] in the stability of molecules, its importance in organic chemistry does not seem to be fully appreciated. In the recent monograph on Molecular Rearrangements by Porter,[2] there are so many examples of the influence of the inter-kernel repulsions, that it appears desirable to formulate a statement which will be of assistance in interpreting these complex organic reactions.

The energy of the molecule is, of course, the sum of the energies of the repulsions and attractions of the electrons and atomic kernels and at present it is quite impossible to evaluate all these energies. Indeed, our one bit of quantitative information is the energy of repulsion of the atomic kernels. In this case, since these kernels are small in comparison to the interatomic distances, the energy of repulsion between two kernels of charges e and e', separated by a distance, d, is $E = ee'/d$. The interatomic distances are capable of determination from crystal structure data and as the kernel is, by definition, the atom minus the valence electrons, its charge is equal to the number of valence electrons possessed by the neutral atom.

The magnitude of this repulsive energy is very great, for example, that between carbon and nitrogen in aniline is over two million calories. In a stable molecule this repulsion is overcome by the mutual attractions of the kernels for the electrons or electron pairs of the two atoms, but it seems obvious that if any arrangement of the molecule is possible in which this repulsion force may be greatly decreased and at the same time satisfy equally well the electron affinities of all the atoms, such a rearrangement might take place. For example, in the change of methylaniline into p-toluidine, N—C and C—H bonds are changed to N—H and C—C bonds. In the resulting molecule the atoms all possess the same number of electrons which they had before the rearrangement but the energy of repulsion has been decreased by approximately 400,000 cal. The free energy of the change is very much less than this, so there must also be a decrease in the energy of the bonding electrons. Although the latter cannot be calculated, it seems probable that it should always be less than the decrease in the repulsion energy.

In order to test this assumption, a survey has been made of all the re-

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[1] *See* Pauling and Hendricks, THIS JOURNAL, 48, 641 (1926); Latimer and Rodebush, *ibid.*, 42, 1419 (1920).

[2] Porter, "Molecular Rearrangements," The Chemical Catalog Co., Inc., New York, 1928.

arrangements listed by Porter and the reactions are classified according to the bonds broken and formed. The values used in calculating the increase or decrease of the repulsion energies are summarized in Table I. These energies are based upon interatomic distances determined by x-ray diffraction data and molecular moments from band spectra data. It is to be expected that each type of bond should be only approximately constant in various compounds and in general variations of 10 and 15% in the interatomic distances are found. The values for the interatomic distances which have been employed are taken from summaries by Pauling,[3] Huggins[4] and Birge.[5]

The various types of rearrangements and their repulsion energies are summarized in Table I. In the following discussion the numbers refer to the types as listed in Table II.

TABLE I

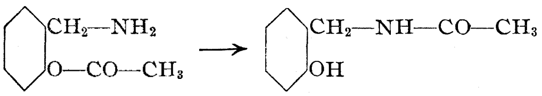
REPULSION ENERGIES OF ATOMIC KERNELS IN VARIOUS BONDS[a]

Bond	Dist. bet. atomic centers, Å.	Repulsion energy, kilocal.	Bond	Dist. bet. atomic centers, Å.	Repulsion energy, kilocal.
C—H	1.20	550	N—N	1.40	2950
C—C	1.52	1700	N=N	1.21	3400
C=C	1.47	1750	N—O	1.35	3650
C—N	1.46	2250	N=O	1.20	4100
C=N	1.20	2750	N—S	1.65	3000
C—0	1.41	2800	N—Cl	1.64	3500
C=O	1.29	3050	N—Br	1.79	3200
C—S	1.71	2300	O—H	1.05	940
C—Cl	1.70	2700	O—O	1.30	4550
C—Br	1.85	2500	O=S	1.56	3800
N—H	1.15	715	0—Cl	1.52	4550

[a] Instead of these values, as a rough approximation, applicable in most cases, the interatomic distances may be assumed constant and the energies expressed in terms of the product of the kernel charges. For example, in the N—C and C—H rearrangement to N—H and C—C given above (5 × 4) + (4 X 1) = 24 and (5 X 1) + (4 × 4) = 21. This decrease of 3 units corresponds to about 400 kilocal. in this example.

Rearrangements Taking Place with a Decrease in Repulsion Energy.—(1) The example of methylaniline has been given above. Other rearrangements of this type are methylenedi-p-tolylimide to diaminoditolymethane, ethylphthalimidoacetate to a derivative of oxycarbostyril, diacylanilides to acylamino ketones and N-acetylpyrrole to b-acetylpyrrole.

(2) There are a number of reactions similar to the following



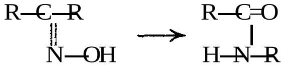
Pauling, Z. *Krist.*, 67, 377 (1928).

Huggins, *Phys. Rev.*, 28, 1086 (1926).

[5] Birge, "International Critical Tables," Vol. V, 1929, p. 409.

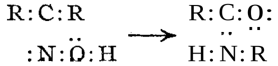
Other examples are: the ethyl ester of formanilide to ethylphenylformamide and the rearrangement of the triazoles.

(3) Many examples of the Beckmann rearrangement



$$\begin{array}{c} R-C-R \\ \| \\ N-OH \end{array} \longrightarrow \begin{array}{c} R-C=O \\ | \\ H-N-R \end{array}$$

It seems probable that these double bonds between carbon and the more electronegative atoms are not to be interpreted as two electron pairs, but rather as carbon with a coördination number of three, as in carbonate. However, the interatomic distances are less in the double bond and there is doubtless considerable distortion of the octet of the nitrogen and oxygen. The electron formula then would be

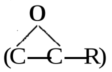


$$\begin{array}{c} R:C:R \\ :N:\ddot{O}:H \end{array} \longrightarrow \begin{array}{c} R:C:\underset{\cdot\cdot}{O}: \\ H:\overset{\cdot\cdot}{N}:R \end{array}$$

This interpretation is important in the generalization which we wish to draw later. Another example is the conversion of fluorenone oxime to phenanthridone.

TABLE II

CHANGE IN INTER-KERNEL REPULSION ENERGIES IN VARIOUS MOLECULAR REARRANGEMENTS

	Bonds rearranged	Energies in kilocal.
(1)	(C—N + C—H) to (N—H + C—C)	− 385
(2)	(O—C + N—H) to (O—H + N—C)	− 225
(3)	(C—C + N—O—H) to (C=O + H—N—C)	− 275
(4)	(=S=O + C—H) to (=S + C—O—H)	− 360
(5)	(O—C + =S) to (=0 + S—C)	− 500
(6)	(O—C + C—H) to (O—H + C—C)	− 710
(7)	(N—Cl + C—H) to (N—H + C—Cl)	− 635
(8)	(C—N=C) to (C—C=N)	− 550
(9)	(N—S + C—H) to (N—H + C—S)	− 535
(10)	(C—Br + N—Cl) to (C—Cl + N—Br)	− 100
(11)	(N—N + 2(C—H)) to (C—C + 2(N—H))	−2300
(12)	(N—N + C—H) to (N—H + C—N)	− 535
(13)	(N—0 + C—H) to (C—O + N—H)	− 685
(14)	 to (R—C—C=O)	−2550
(15)	(C—S + ≡N) to (=S + =N—C)	− 50
(16)	(C—C′ + C″—C‴) to (C—C″ + C′—C‴)	0
(17)	(C—N + N′—H) to (C—N′ + N—H)	0
(18)	(C—X + C′—H) to (C′—X + C—H)	0
(19)	(C—C + —N) to (C—N= + C=)	+ 550
(20)	(N—C + =0) to (—N= + O—C)	+ 450

(4) The rearrangements of amine sulfoxides.

(5) Thioncarbamates to thiol derivatives.

(6) A great many examples of which the rearrangement of the allyl ethers is typical.

(7) The rearrangement of acyl halogen aminobenzene.

(8) The conversion of ethyl isocyanide to propionitrile.

(9) Several cases in the sulfonic acids and amides of sulfonic acids.

(10) The rearrangement of brominated benzenediazonium chloride.

(11) The benzidine type of rearrangement.

(12) Numerous cases of the nitroso-amines and hydrazines.

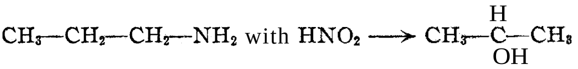
(13) One example is β-phenylhydroxylamine to p-aminophenol. Other examples are the rearrangements of the amine oxides and the conversion of quinoline by alkyl halides to carbinol bases.

(14) This change appears to be an intermediate step in some of the pinacol rearrangements. Although the definite formation of the intermediate ethylene oxide may not always occur in these reactions, the free bonds on the oxygen and carbon which result from the splitting off of water are potentially equivalent to the oxide formation. Other rearrangements essentially the same are benzil to benzilic acid and benzoin to diphenylacetic acid.

(15) The change of methyl thiocyanate to methyl isothiocyanate, R—S—C—N $\longrightarrow$ R—N=C=S. Although in the older bond theories of organic chemistry this change might be interpreted as involving a shift in the number of electrons on each atom, the probable electron formulas do not indicate that such is the case, that is, the structure is similar to that of carbon dioxide

$$R:\ddot{S}:C:\ddot{N}: \longrightarrow :\underset{\cdot\cdot}{\ddot{S}}:C:\underset{\cdot\cdot}{\ddot{N}}:R$$

Reactions Involving no Change in Repulsive Energy.—(16) There are a number of examples of shifts of carbon to carbon bonds. These often take place during reactions, that is, when the molecule is in a highly activated state, as in the following



$$CH_3—CH_2—CH_2—NH_2 \text{ with } HNO_2 \longrightarrow CH_3—\underset{OH}{\overset{H}{C}}—CH_3$$

As might be expected if the two possible forms have nearly the same energy the product is a mixture of the two forms. In some examples, however, symmetry and steric effects also doubtless play a part in determining the more stable form. Carbon to carbon shifts also occur in unsaturated compounds, the rearrangement giving forms which decrease the electrical moment of the molecule. An example of such a change is found in the reduction of methyl *tert.*-butyl ketone to tetramethylethylene.

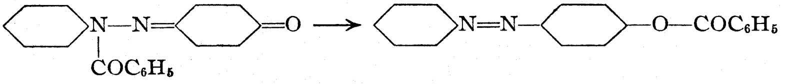
(17) One of the simpler examples is the change of (NHR)(NR—NH$_2$)C=O to (NHR)(NH—NHR)C=O. Although this reaction involves no change in the kernel repulsions in the various bonds, it might be pointed out that the repulsion of the R group for all of the neighboring atoms appears to be decreased by this rearrangement,

(18) There are several examples of the shift of a halogen from one carbon to another.

Rearrangements Involving an Increase in the Repulsion Energy.—(19) Porter[6] considers that the best theory of the Hofmann and Curtius rearrangements is the formation of an intermediate compound containing an unsaturated nitrogen which then rearrange with the transfer of a carbon radical to the nitrogen. For example, R—CO—NHBr ⟶ R—CO—N ⟶ R—N=C=O, or **in** electron formulas, $R:\underset{:N:}{\underset{..}{\overset{..}{C}}}:\underset{..}{\overset{..}{O}}: \longrightarrow R:\underset{..}{\overset{..}{N}}:C:\underset{..}{\overset{..}{O}}:$. If this mechanism is correct the change involves an increase in the repulsion energies but it also involves a change in the number of electrons on the nitrogen, that is, it takes place because the more electronegative nitrogen will gain electrons at the expense of the carbon. However, there is a possibility that the first step is the interchange of the R and Br and in this case there is first a decrease in the repulsion energy.

In addition to the many examples of the Hofmann rearrangement, certain benzene-azo-acetyldibenzoylmethane changes may be considered as involving a transfer of electrons from carbon to nitrogen.

(20) The rearrangement of the quinonehydrazones



takes place with an increase in the repulsion energy of the kernels. Although the shift appears to involve complicated electron rearrangements, the evidence regarding the electron structures of benzene and quinone does not permit a complete interpretation.

The keto-enol tautomerism of the acetoacetic acid esters seems at first sight to be a case of increasing repulsion energies, since a hydrogen may shift from carbon to oxygen, O=C—C—H to H—O—C=C. However, the sum of the repulsion energies, including the double bonds, as calculated from Table I, for the two forms gives only a small positive value and at ordinary temperatures the equilibrium favors the ketone as predicted. Moreover, the rearrangement must involve some redistribution of electrons in the formation of the double bond between the carbons,

Conclusions and Summary

The results of this detailed study of the various types of organic rearrangements show: (1) the great majority of these changes take place with a decrease in the inter-kernel repulsion energy. (2) A few occur with no change in repulsion energy. These often result from a state of high activation of the molecule and the product is a mixture of the two forms. **(3)** Rearrangements with an increase in repulsion energy are rare

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[6] Porter, ref. 2, p. 16.

and invariably accompanied by complex redistributions of electrons in the molecule.

These observations are entirely in accord with the following premise: *if there are a number of possible arrangements of the atoms in a molecule which have the same number of electrons per atom and which satisfy equally well the tendencies of the more electronegative elements to complete their octets of electrons, that form will be the most stable which gives a minimum of repulsion between the atomic kernels.*[7]

BERKELEY, CALIFORNIA

THE MECHANISM OF HOMOGENEOUS GAS REACTIONS. II. THE ABSORPTION SPECTRUM OF NITROGEN PENTOXIDE AND ITS METHOD OF DECOMPOSITION

BY H. C. UREY, L. H. DAWSEY AND F. O. RICE

RECEIVED MARCH 8, 1929 PUBLISHED NOVEMBER 8, 1929

The thermal and photochemical dissociation of nitrogen pentoxide has been the subject of a number of important investigations during the past few years. Daniels and Johnston[1] showed that the thermal dissociation followed a unimolecular law and that the temperature coefficient of the velocity constant gave a mean value for the energy of activation calculated from the Arrhenius equation of 24.7 kg. cal. The average deviation of this quantity is 0.42 kg. cal. They illuminated their nitrogen pentoxide with infra-red radiation of approximately $\lambda = 1.16\mu$, corresponding to the energy values of the heat of activation, but found that there was no increased reaction due to illumination. Later investigations[2] have provided ample confirmation that neither this nor any other wave length in the infra-red causes appreciable decomposition of nitrogen pentoxide. Daniels and Johnston illuminated nitrogen pentoxide and a mixture of nitrogen pentoxide and nitrogen peroxide contained in a glass vessel by direct sunlight and found that nitrogen pentoxide decomposes only in presence of nitrogen peroxide. They isolated the region from 4000 to 4600 Å. (blue light) by filters and found that these were active wave lengths. By interposing a filter of nitrogen peroxide they showed that decomposition did not take place. Fazel and Karrer[3] proposed that the effect was due to the absorption of light by the nitrogen peroxide molecule, which then transferred its energy by a collision of the second kind to the nitrogen pentoxide molecules.

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[7] These observations are also in accord with the conclusion of Pauling and Hendricks (ref. 1) regarding the stability of certain inorganic isomers.

[1] Daniels and Johnston, THIS JOURNAL, 43, 53, 72 (1921).

[2] Daniels, *ibid.*, **48**, 607 (1926); Taylor, *ibid.*, **48**, 577 (1926); Mayer, *ibid.*, **49**, 3933 (1927).

[3] Fazel and Karrer, *ibid.*, 48, 2837 (1926).

The effect of light on nitrogen peroxide has been studied by Norrish,[4] who concluded that there is an equilibrium established according to the equations

$$NO_2 + h\nu \longrightarrow NO_2'$$
$$NO_2' + NO_2 \longrightarrow 2NO + O_2$$
$$2NO + O_2 \longrightarrow 2NO_2$$

He then assumed that the photochemical decomposition of nitrogen pentoxide was a secondary dark reaction represented by the equation

$$NO + N_2O_5 \xrightarrow{\text{Dark}} 3NO_2$$

Dickinson and Baxter[5] confirmed Norrish's view that gaseous NO_2 is decomposed by light into NO and O_2; they determined the quantum yield of the reaction at sufficiently low pressures that the rate of recombination of NO and O_2 was negligibly slow. The quantum yields secured were 0.0046 at 4350 Å., 0.36 at 4050 Å. and 0.77 at 3660 Å.

Busse and Daniels[6] then showed that nitric oxide and nitrogen pentoxide react very rapidly to give nitrogen peroxide according to the last equation; they also showed that the addition of inert gases to the nitrogen pentoxide–nitrogen peroxide mixture does not inhibit the photochemical decomposition. This indicates that the mechanism of Fazel and Karrer is not the correct one, because quenching of the excited nitrogen peroxide molecules should recur under these conditions. It appears that the mechanism is the photochemical production of nitric oxide molecules, which then react with the nitrogen pentoxide molecules to form nitrogen peroxide.

Recently Harris[7] has studied the absorption spectra of nitrogen peroxide and nitrogen tetroxide. The absorption spectrum of NO_2 molecules consists of a large number of bands, many with fine structure, from 6000 to 2250 Å.; the absorption due to N_2O_4 in the gaseous phase is continuous. Two bands, one with a maximum at 3500 Å. and another with a maximum further in the ultraviolet, merge at high pressures of N_2O_4 into one continuous band which extends from 4000 Å. into the far ultraviolet.

The Absorption Spectrum of Nitrogen Pentoxide.—Since the ultraviolet absorption spectrum of nitrogen pentoxide has not been studied previously, we have investigated it and present the results in this paper. We have photographed the ultraviolet absorption spectrum and found it to be continuous, with no evidence of a banded structure. The absorption begins at about 3050 Å. and extends into the Schumann region. Nitrogen pentoxide was distilled through a long absorption cell at low pressures. Any gases produced by photochemical decomposition were removed by a

[4] Norrish, J. *Chem. Soc.*, 130, 761 (1927).

[5] Dickinson and Baxter, THIS JOURNAL, 50, 774 (1928).

[6] Busse and Daniels, *ibid.*, 49, 1257 (1927).

[7] Harris, *Proc. Nat. Acad. Sci.*, 14, 690 (1928).

vacuum pump and liquid–air traps. Weak bands due to nitrogen peroxide were always present on our plates when the experiments were carried out in this way. These weak bands disappeared when the nitrogen pentoxide was treated with ozone before taking the absorption spectrum, but the continuous spectrum was unchanged. Light of wave length longer than 3000 or 3050 Å. is always transmitted.

The Energy of Dissociation of Nitrogen Pentoxide.—If we assume that the Franck theory for the dissociation of diatomic molecules by light can be applied to these more complicated molecules, it leads to the conclusion that the molecule is disrupted into two or more fragments by the absorption of light. The heats of dissociation of nitrogen pentoxide into nitrogen dioxide and oxygen or nitrogen dioxide, nitric oxide and oxygen are

$$N_2O_5 = 2NO_2 + \frac{1}{2}O_2 - 16.0 \text{ kg. cal.}$$

$$N_2O_5 = NO_2 + NO + O_2 - 27.7 \text{ kg. cal.}^{8}$$

Taking the heat of dissociation of oxygen[9] as 160,000 cal., we obtain for the heat of dissociation of nitrogen pentoxide into two molecules of dioxide and an atom of oxygen the value

$$N_2O_5 = 2NO_2 + O - 96 \text{ kg. cal}$$

Nitrogen pentoxide commences to absorb at 3050 Å., which is equivalent to 93.2 kg. cal.; this agrees very closely with the last equation and indicates that the primary photochemical reaction may be dissociated into an oxygen atom and two nitrogen dioxide molecules. It is, of course, possible that the primary photochemical reaction is any reaction which has an energy change less than 93.2 kg. cal., corresponding to the long wave length limit of the continuous spectrum of nitrogen pentoxide; several diatomic molecules are known whose energy of dissociation is considerably less than that corresponding to the wave length at which they begin to absorb.

The Mechanism of the Thermal Dissociation of Nitrogen Pentoxide.—The energy of activation for the thermal decomposition is well established as 24.7 kg. cal. and accordingly[10] this is equal to the difference between the mean energy of the molecules which react and the mean energy of all the molecules. This is very close to the amount of energy necessary to dissociate N_2O_5 into NO_2, NO and O_2, leaving these molecules with only a small amount of energy. Using the I.C.T. values for the energies of formation we find that

$$N_2O_5 = NO_2 + NO + O_2;\ \Delta E = 29.0 \text{ kg. cal.}$$

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[8] "International Critical Tables," Vol. 5, p. 178.

[9] Birge and Sponer, *Phys. Rev.* (N. S.), 28, 259 (1926). Birge, *Phys. Rev.*, 34, 1062 (1929) has recently revised the value for the heat of dissociation of oxygen. His suggested value will change the calculated energy change of the reaction $N_2O_5 = 2NO_2 + O$ to $-\sim 85$ kg. cal. This does not disagree with our conclusions.

[10] See Tolman, THIS JOURNAL, 47, 2657 (1925).

This is the energy at constant volume required to produce NO_2, NO and O_2 molecules having the mean translational, rotational and vibrational energy at 18° from an N_2O_5 molecule also having the mean energy at this temperature. If an excited N_2O_5 molecule decomposes during the time of free flight, its translational energy must appear as translational energy of the dissociated molecules in order that the linear momentum may be conserved. Therefore the NO_2, NO and O_2 molecule produced in this way must have this much translational energy, namely, about 0.6 kg. cal., but may have no more translational energy and no rotational or vibrational energy. Using the heat capacity data for these gases from the I.C.T., assuming that the heat capacity of NO_2 is the same as that of CO_2 and also assuming that the heat capacity, C_v, is constant to absolute zero, the total energy of vibration, rotation and translation of these molecules is found to be about 4.8 kg. cal. Subtracting from 29.0 and adding the 0.6 kg. cal. of translational energy, we find that the energy required to decompose the average N_2O_5 molecule at 18° to NO_2, NO and O_2 having no vibrational or rotational energy and the 0.6 kg. cal. of translational energy is 24.8 kg. cal. This agrees very closely with the energy of activation, namely, 24.7 kg. cal., and since either may be in error by considerable amounts, this calculation shows that, so far as energy relationships are concerned, the N_2O_5 molecule may undergo a primary unimolecular dissociation into these three products.

It seems possible that the dissociation of nitrogen pentoxide is analogous to radioactive decomposition as discussed recently by Gurney and Condon.[11] Applying their ideas to the dissociation of nitrogen pentoxide we can say that it is possible that sufficient energy may be localized in the right degree of freedom to cause dissociation of the molecule and yet the molecule will exist in a quantized steady state for a finite length of time and then spontaneously dissociate, the time of dissociation being determined by pure probability.

Another possible mechanism would be the dissociation from a steady state in which the energy is not localized in the particular degree of freedom involved in the dissociation. This case would be similar to the dissociation of the excited hydrogen molecule into two normal atoms as proposed by Rlackett and Franck[12] to account for the continuous hydrogen spectrum. The hydrogen molecule in the $2^3\Sigma$ state spontaneously dissociates[13] into two normal atoms and the energy of excitation of the hydrogen molecule appears as kinetic energy of translation of the hydrogen atoms. This is essentially the theory proposed by Rice and Ramsperger and by Kassel.[14]

The present authors do not believe that any evidence presented as yet

[11] Gurney and Condon, *Nature*, **122**, 439 (1928).

[12] Blackett and Franck, *Z. Physik*, **34**, 389 (1925).

[13] See Winans and Stueckelberg, *Proc. Nat. Acad. Sci.*, **14**, 867 (1928).

[14] Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); 50,617 (1928); Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

will permit us definitely to decide between these two mechanisms; there is also the possibility that there are other mechanisms which will give a unimolecular rate.

Summary

1. The absorption spectrum of nitrogen pentoxide has been measured and shows continuous absorption commencing at 3050 Å. and extending to the far ultraviolet.

2. The long wave length limit of this continuous spectrum corresponds very closely to the energy change in the reaction $N_2O_5 = 2NO_2 + O$ and indicates that this may be the primary photochemical reaction.

3. The mechanism of the thermal decomposition has been discussed and two possible mechanisms have been pointed out which are analogous to the radioactive decomposition of nuclei and the spontaneous dissociation of the excited hydrogen molecule.

BALTIMORE, MARYLAND

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

THE HEAT CAPACITY OF NITRIC OXIDE FROM 14°K. TO THE BOILING POINT AND THE HEAT OF VAPORIZATION. VAPOR PRESSURES OF SOLID AND LIQUID PHASES. THE ENTROPY FROM SPECTROSCOPIC DATA

BY H. L. JOHNSTON AND W. F. GIAUQUE

RECEIVED MARCH 11, 1929 PUBLISHED NOVEMBER 8, 1929

In a recent paper[1] the entropy of oxygen has been discussed. This was particularly interesting due to the effect of two spinning electrons. **In** this paper nitric oxide will be considered.

Jenkins, Barton and Mulliken[2] have measured the fine structure of the β-bands of nitric oxide and have given a very satisfactory interpretation of them. It is evident from their work that the nitric oxide gas molecules exist in a double electronic level under ordinary conditions. This arises from one-half unit of electronic spin which may couple with or against the one unit of electronic angular momentum which is directed along the figure axis of the molecule. The energies and probabilities associated with the rotation of the molecule as a whole are much influenced by the nature of the electronic coupling and are correspondingly different for the two cases referred to above.

The unbalanced angular momentum responsible for the strong paramagnetism of the nitric oxide molecule has a considerable effect on the entropy to be considered in the latter part of this paper. The theoretical treatment of the magnetic susceptibility of the nitric oxide molecule has

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

[2] Jenkins, Barton and Mulliken, Phys. Rev., 30, 150 (1927).

been considered by Van Vleck,[3] who arrived independently at the same electronic configuration for the molecule as was indicated by the band spectra. The above spectroscopic data and interpretation make possible the calculation of a very accurate value of the entropy.

The object of the present investigation was to obtain reliable heat capacity data for solid and liquid nitric oxide from the boiling point of nitric oxide to temperatures obtainable with liquid hydrogen under reduced pressure. Our object was to determine whether the third law of thermodynamics, as ordinarily used, would give a value for the entropy agreeing with that calculated from spectroscopic data. In the light of opinions advanced in earlier papers[4,5] it may be expected that for some substances, due to lack of thermodynamic equilibrium or to effects occurring close to the absolute zero, or both, the integral $\int C_p \mathrm{d} \ln T$ might give too small a value.

The entropy of nitric oxide from the calorimetric data is considerably lower than that obtained from spectroscopic data although the entropy calculated from the latter may be considered reliable.

Preparation and Purification of Nitric Oxide.—The difficulty of preparing pure nitric oxide has been recognized by various investigators and probably accounts for the discordant data on the physical properties. Adwentowski[6] expressed doubt that the gas could be prepared in a high state of purity. Difficulty arises from the fact that all processes for the preparation of the gas depend on the reduction of either NO_3^- ion or of NO_2^- ion and the NO produced always contains traces of other oxides or reduction products not easily removed, particularly NO_2, N_2O_3 and N_2. A comparatively large amount of nitric oxide was desired in a higher state of purity than any previously obtained in order to fix certain physical constants with great accuracy. A careful study was made to determine the best method of preparation and purification. The investigations of Moser[7] indicated that the best method for the preparation is that described by Winkler.[8] A dilute solution of sulfuric acid is dropped into a solution of potassium nitrite and potassium oxide. The nitric oxide is produced by the reaction $2NO_2^- + 4H^+ + 2I^- = 2NO + I_2 + 2H_2O$. When the preparation is carried out under proper conditions and the product is passed through wash bottles containing in turn sulfuric acid and potassium hydroxide solutions, Moser finds that nitric oxide of 99.8% purity may be produced. Germann[9] showed that fractional distillation was usually more

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[3] Van Vleck, *Phys. Rev.*, 31, 587 (1928).

[4] Giauque, THIS JOURNAL, 49, 1870 (1927).

[5] Giauque and Johnston, ibid., **50**, 322 (1928).

[6] Adwentowski, *Anz. akad. Wiss. Krakau*, S142 (1909).

[7] Moser, *Z. anal.* Chem , **50**, 401 (1911).

[8] Winkler, *Ber.*, 34, 1408 (1901).

[9] Germann, *J. Phys. Chem.*, **19**, 437 (1915).

effective for final purification than the use of chemical purifying agents, Gray,[10] however, has shown that the usual methods of fractionation become ineffective for nitric oxide and describes an effective means of distillation which relies for its efficacyon the high solubility of the oxides in liquid nitric oxide and their low vapor pressures at the boiling point of nitric acid. Nitrogen is best removed by evacuating the freshly sublimed solid.

The preparation and purification were based on the suggestions above. The measurements were carried out with three different preparations of nitric oxide. In Preparation I a six-liter pyrex round-bottomed reaction flask was employed. This could be emptied or filled with fresh reagents through a pyrex stopcock without contamination with air. It was initially half filled with a nearly concentrated solution made by dissolving 5 kilograms of potassium nitrite and 2.5 kilograms of potassium iodide in 15 liters of distilled water. Nitric oxide was generated by dropping a 50% solution of sulfuric acid from an acid reservoir. Regulation of stopcocks controlled the rate at which the gas was generated. During operation the mixture was stirred by an electromagnetic stirrer. Platinum–iridium in the form of a wire spring, which served to prevent injury to the apvaratus, was the only material other than pyrex glass in contact with solution or evolved gas. It was necessary to refill the reaction flask several times in the course of a preparation in order to obtain the amount of nitric oxide desired. Some annoyance was experienced in this operation due to the precipitation of large amounts of iodine, and to the formation of hard crystals of potassium sulfate which clogged the drainage tube. Accordingly in Preparations II and III a 20-liter bottle was substituted, which held enough of the reagents to avoid the necessity of refilling. This was made of common glass and was fitted with a two-holed rubber stopper through which projected the dropping stem from the acid reservoir and the outlet tube for the gas. To make certain that it was vacuum tight the stopper was covered externally with de Khotinsky cement. The solution was unstirred but the gas generated was subjected to one more fractionation in the later stages of purification than Preparation I and, as the data will show, there was no appreciable difference in purity between Preparation I and Preparations II and III.

As a practical precaution, the 20-liter bottle was placed in a small barrel to avoid danger in case it should collapse when evacuated. This precaution was found necessary for on one occasion a similar bottle which had been previously tested and frequently evacuated collapsed under a vacuum and threw pieces of glass with considerable violence.

From the generator the crude gas entered the purifying train. It was first bubbled through a tall column of 90% sulfuric acid and then through a tall column of 50% potassium hydroxide solution. Both columns contained glass beads to break up the bubbles. Next was included a trap immersed in a bath of solid carbon dioxide and ether. The principal purpose of this trap was to remove the bulk of the moisture but it also served to condense a further portion of the higher oxides that might have passed through the potassium hydroxide. The gas was condensed in a bulb surrounded with liquid air. When sufficient nitric oxide had collected, the generator was stopped, and the gas was distilled, passing on its way through about two meters of tubing packed alternately with phosphorus pentoxide and plugs of glass wool, the first and last portions being discarded. Following this the nitric oxide was distilled into a bubbling bulb until it had collected to a depth of four or five centimeters, after which the depth was kept constant by regulating the height of liquid air in an unsilvered Dewar flask while

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[10] Gray, J. Chem. *Soc.*, **87**, 1601 (1905).

the remainder was slowly bubbled through in accordance with the suggestion of Gray, mentioned above. Two such stages of bubbling were included in each cycle, the liquid in the first stage, with the relatively non-volatile other oxides of nitrogen being discarded, and the liquid remaining in the second bubbling bulb being transferred to the first to serve as the initial concentrate for the next operation. The nitric oxide was then solidified, pumped for several minutes, sublimed under a pressure of about 5 cm. of mercury and pumped again for several minutes. Finally the nitric oxide was returned to the beginning of the cycle and the distillation and sublimation process repeated. This cycle was carried through three times for Preparation I and four times for Preparations II and III. During the process about 450 cc. of liquid nitric oxide initially collected was reduced to about 150 cc. of purified liquid. The middle 105 or 110 cc. was then distilled into the calorimeter. Except during the sublimation process the pressures in the generator and purifying line were kept close to atmospheric. The pressures were observed on five manometers, which also served as safety valves in case of need.

Great care was taken to avoid contamination by air since Moser[7] had shown that small amounts of air had a catalytic action in the decomposition of nitric oxide. Except for the reaction bottle and its rubber stopper the entire generating and purifying system was constructed of pyrex glass with fused joints. The stopcocks used were special high vacuum stopcocks and were greased with rubber stopcock grease[11] previously saturated with nitric oxide gas at 150°. Before the liquid reagents were added to the generator or purifying columns, the entire line was evacuated to a pressure of about 10^{-5} mm of mercury and was pumped for several days with occasional sparking and heating to remove adsorbed gases from the phosphorus pentoxide and from the walls of the glass line. All solutions were boiled to expel air. After supplying the reagents the system was again evacuated for several hours. A slow stream of nitric oxide was passed through the line for several minutes before any was collected. The gas was generated slowly in order to avoid loss of efficiency in the purifying columns. For the same reason distillation and sublimation were carried out at a moderate rate. With continuous day and night operation a period of four or five days was consumed from the time that the generator was started until the nitric oxide was distilled into the calorimeter.

No analyses of the gas were made since accurate melting point and heat capacity data provide a more sensitive test of impurity than are given by chemical analysis. Following the presentation of the data there will be given a full discussion of the question of purity.

Heat Capacity Measurements and Data.—The calorimetric measurements and the measurements of the amounts of material were carried out in the same manner and with the same apparatus described for the measurements on oxygen.[1] The discussion given in the latter work relative to the sources of error and treatment of the data applies practically without change in the work on nitric oxide. Since the amount of gas was measured volumetrically, we made use of certain physical constants of nitric oxide which are given below. The molecular weight was taken as 30.008.[12] The density used was 1.34018 as given by Scheuer.[13] The

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[11] "Handbook of Chemistry and Physics," The Chemical Rubber Co., Cleveland, 1922, p. 654.

[12] Thirty-Fourth Annual Report of the Committee on Atomic Weights, THIS JOURNAL, 50, 603 (1928).

[13] Scheuer, *Sitzb. Akad. Wiss. Wien,* 123, 2A, 1029 (1914).

mean coefficient of expansion between 0 and 25° as given by Leduc[14] is 0.003677. The coefficient of deviation from Boyle's law per atmosphere is given by Batuecas[15] as —0.00112.

Two series of measurements, described as IIIa and IIIb, were carried out to determine the heat capacities of solid and liquid nitric oxide. Both were made with Preparation III. Within each series the measurements were made in order of rising temperature and between the two series a small measured amount of nitric oxide was removed from the calorimeter in the process of removing the plug of solid nitric acid which had distilled into the glass tube above the calorimeter during the period of recooling. The two series of measurements taken together covered the temperature interval from about 14.3 to about 122.1°K. The data are recorded in Table I, in which the first column gives the serial number of the run, the second column the mean absolute temperature, the third column the temperature interval covered and the fourth the heat capacity in calories per mole per degree.

TABLE I

HEAT CAPACITY OF NITRIC OXIDE

Molecular weight, 30.008. Series IIIa 3.7691 moles. Series IIIb 3.7476 moles

Series	T, °K.	AT, °K.	C_p/mole in cal./deg.	Series	T, °K.	AT, °K.	C_p/mole in cal./deg.
IIIb	15.57	2.447	0.935	IIIb	83.83	4.949	7.516*
IIIb	17.75	1.733	1.303	IIIb	88.96	4.996	7.795
IIIb	19.51	1.685	1.590	IIIb	94.04	4.998	8.130
IIIb	22.27	3.006	1.964	IIIb	98.51	3.773	8.397
IIIb	25.36	2.960	2.389	IIIb	102.55	4.153	8.713
IIIb	28.59	3.399	2.807	IIIa	106.39	2.409	9.033
IIIb	32.08	3.490	3.274	IIIb	106.65	3.882	9.120
IIIb	35.50	3.375	3.691	IIIa	108.39	1.525	9.456
IIIb	39.20	3.930	4.060				
IIIb	43.51	4.679	4.481	Melting point at 109.49°K.			
IIIb	48.16	4.621	4.895	IIIb	112.81	2.844	16.067
IIIb	52.64	4.324	5.543	IIIa	114.01	3.298	16.362
IIIb	57.25	4.796	5.686	IIIb	115.79	2.896	16.915
IIIb	62.32	5.319	6.016	IIIa	117.35	3.293	17.329
IIIb	67.90	5.515	6.392	IIIb	118.86	3.125	17.935
IIIb	73.24	5.030	6.760	IIIa	120.56	3.024	18.667
IIIb	78.84	4.942	7.158				

The results tabulated above are also shown graphically by the dark circles in Fig. 1. The results of all runs have been tabulated and plotted, but the value marked with an asterisk in this table is known definitely to be in error due to improper experimental conditions for which adequate corrections could not be applied. The point at 52.64° may be in error although a careful study of data taken in that and adjacent runs failed

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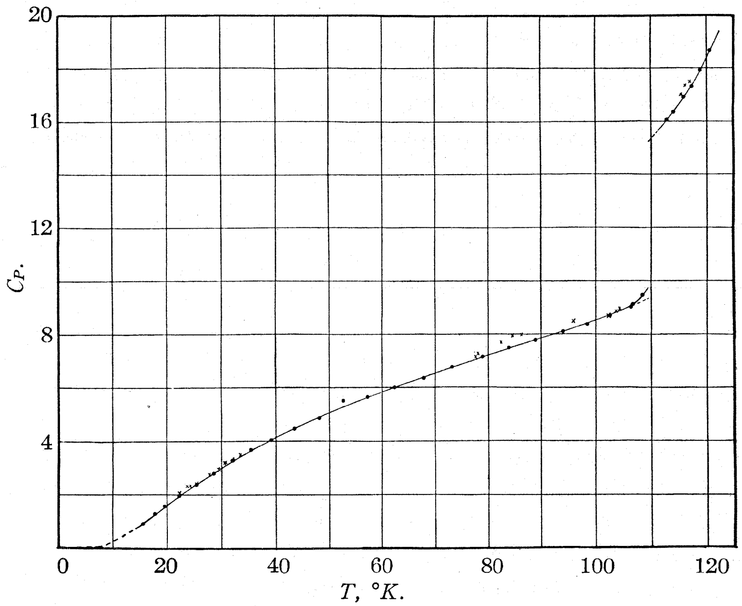
[14] Leduc, Ann. ***Physik,*** 5, 180 (1916).

[15] Batuecas, *Anales soc. españ. fís. quím.*, **20,** 441 (1922).

to reveal any factor to which might be assigned an error within reasonable limits sufficient to account for the deviation. It is possible that a transition of very small energy change has been included. A transition heat of about 1.3 calories per mole would account for this point. It is also possible that the point falls on the maximum of a gradual transition. This region could readily have been studied in detail had this situation been suspected but unfortunately the calorimeter was emptied before it was discovered. From the standpoint of the entropy calculation this is immaterial since the area concerned, if real, would affect the entropy by only 0.02 of an entropy unit.



●, This Research; ×, Eucken and Karwat.

Fig. 1.—Heat capacity in calories per mole of nitric oxide.

The short interval runs taken in Series IIIa just below the melting point were for the purpose of evaluating the degree of impurity and will be discussed in a later paragraph. The sharp rise in the solid curve is assumed to be due to the influence of premelting and the dotted curve represents the extrapolation for the pure solid.

For the sake of comparison the results of Eucken and Karwat[16] have been plotted and are represented by crosses. It will be observed that their values are in general higher than ours and show large deviations among themselves. Compared with the curve of Fig. 1, their results for solid nitric oxide from 22 to 34° show an average deviation of 2.3% with a maxi-

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[16] **Eucken** and Karwat, *Z. physik. Chem.*, **112, 467** (1924).

mum deviation of 6%. In the region from 82 to 104°, their results differ from the curve by 2.5% on the average and show a 5% maximum deviation. These deviations are somewhat larger than the probable error claimed by those authors, who believed their values for solid nitric oxide to contain no larger maximum error than 2% with an average error of only 1%. The points they secured for liquid nitric oxide agree more closely with ours and the deviations are within the limits of error which they claimed.

Among our values, with the exception of these points already discussed, only six of the points above 30° deviate from a smooth curve by more than 0.1 of 1%. Of these only two deviate by more than 0.2 of 1%. It is believed that for the region from 35° to the boiling point the smooth curve represents correct values of C_p to within 0.2 of 1%. Below 35° the accuracy is lessened somewhat, due partly to the lowered heat capacity but principally to the lower temperature coefficient of the resistance thermometer. At 20° the error may be 0.7 of 1% and at 14° may be as large as 2 or 3%.

Melting Point.—The melting point was determined for each of three preparations of nitric oxide. On each occasion readings were taken at intervals of three or four hours over a period of about two days. When constancy of successive readings indicated that thermal equilibrium was attained, a further fraction of the solid was melted and more readings were taken at subsequent intervals. This was done to avoid the influence of impurity in the final value chosen for the melting point, although the data make it evident that very little influence of this sort existed. Table II records the measurements. The data for Preparations I, II and III are arranged in order. Column one indicates the date and approximate hour at which observations were recorded. Column two indicates the approximate percentage melted. Column three records the absolute temperatures determined. These were calculated from the reading of the standard thermocouple soldered to the bottom of the calorimeter. The readings of the thermocouple are ordinarily reproducible to 0.01°, so differences of that amount are without significance in this column. For that reason, there is included in column four the resistance (in ohms) of the gold resistance thermometer wound on the outer surface of the calorimeter. The readings of this thermometer are ordinarily reproducible to 0.001 or 0.002 of an ohm and the resistance at this temperature is changing by almost exactly an ohm per degree. The comparison of resistance is only significant as between values in a single series of measurements, since in the period between the readings on Preparations I and II the wire had been subjected to strain and the calibration changed, and between the measurements of Preparations II and III a new resistance thermometer was wound. These are referred to as thermometers A, A' and B.

TABLE II

MELTING POINT OF NITRIC OXIDE

Date and time		Percentage melted	T, °K. (from thermocouple)	R, ohms, from resist. thermometer
		Preparation I		
12/14/27	4:00 P.M.	Heated into melting point		Thermometer A
	9:00 P.M.	15	109.49	169.402
	12:00 P.M.	15	109.49	169.401
12/15/27	9:30 A.M.	15	109.50	169.397
	9:45 A.M.	Supplied heat		
	2:00 P.M.	50	109.49	169.401
	6:00 P.M.	50	109.50	169.398
	9:30 P.M.	50	109.51	169.402
	12:00 P.M.	Supplied heat		
12/16/27	9:30 A.M.	75	109.49	169.399
		Preparation II		
1/ 6/28	9:00 P.M.	Heated into melting point		Thermometer A'
1/ 7/28	12:30 A.M.	3	109.49	169.437
	2:00 A.M.	Supplied heat		
	7:00 A.M.	50	109.51	169.437
	10:00 A.M.	50	109.48	169.438
		Preparation III		
3/24/28	12:30 P.M.	Heated into melting point		Thermometer B
	9:00 P.M.	5	109.48	.....
	10:00 P.M.	Supplied heat		
3/25/28	11:00 A.M.	50	109.49	173.161
	7:00 P.M.	50	109.53	173.162
3/26/28	10:00 A.M.	50	109.49	173.166
	2:00 P.M.	50	109.51	.....

Accepted value, 109.49 ± 0.05°.

It will be observed that among the temperatures recorded by the thermocouple at various times, only four differ by more than 0.01° from the value chosen as the melting point. In other words, they lie within the precision of the thermocouple to distinguish them. The resistance thermometer likewise shows this constancy of temperature since the extreme readings

TABLE III

TRIPLE POINT DATA FOR NITRIC OXIDE

Observer	T, °K.	*P*, int. cm.
This research	109.49 ± 0.05	16.438 ± 0.004
Henglein and Kruger[17]	109.4	16.57
Goldschmidt[18]	109.88	17.02
Eucken and Karwat[16]	About 110	. .
Adwentowski[6]	112.4	16.8
Olszewski[19]	106.1	13.8

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[17] Henglein and Kruger, *Z. anorg. allgem. Chem.*, **130,** 181 (1923).

[18] Goldschmidt, *Z. Physik,* 20, 159 (1923).

[19] Olszewski, *Compt. rend.,* **100,** 940 (1885).

in any one series differ by only 0.005 of a degree. The chosen value, 109.49°, is then subject only to the uncertainty of temperature scale, which amounts to about 0.05°.

For the sake of comparison, in Table III are listed melting point values reported by various authors. Values of the triple point pressure are also included.

Heat of Fusion.—The heat of fusion was measured in the usual manner. Correction was applied for $\int C_p dT$ and also for the small amount of premelting that had occurred below the temperature at which the energy input was begun. The latter correction was determined from the area between the solid and dotted curves in Fig. 1.

The results are given in Table IV, in which column one gives the amount of material melted (in moles); column two the temperature interval covered; column three the total heat input in calories corrected for all factors except $\int C_p dT$ and the premelting correction referred to above; column four the total of these last two corrections for calorimeter plus contents; and columns five and six the individual values and the mean value of our determinations. The latter value is believed to be correct to within 0.2 of 1%. Both measurements were made with Preparation III. At the bottom of the table, for comparison, are included the experimental values obtained by Eucken and Karwat and the values calculated by Henglein and Kruger and by Goldschmidt from vapor pressure measurements.

TABLE IV

HEAT OF FUSION OF NITRIC OXIDE

Melting Point 109.49°

This research

Amount, moles	Temp. interval	Corr. total heat input, cal.	$\int C_p dT$ + premelting	ΔH, cal. per mole	Mean
3.7691	109 20–112 32	2276.3	204.0	549.8	549.5 ± 1 0
3 7476	109 12–111 02	2177.9	119 8	549 2	

Eucken and Karwat[16]	Henglein and Kruger[17]	Goldschmidt[18]
552	900	539

Heat of Vaporization.—The heat of vaporization was measured in the manner previously described[1] for oxygen. During the determinations the surroundings were maintained at a temperature slightly above the boiling point of the liquid in order to avoid errors due to condensation. By means of the automatic pressure control device referred to in a previous paper,[1] the pressure during the measurements was kept constant at 76 cm. of mercury within 0.1 mm. Heat was supplied to the bottom half of the calorimeter and no measurements were taken after the liquid level had fallen close to the heated portion. They were all made with Preparation III. Energy was supplied for a period of fifty-three minutes in each case. The results are given in Table V, in which the first column gives the number of moles evaporated in each determination, column two the values of the heat of vaporization obtained from the individual measurements and column three the mean value. It will be observed that no individual value differs from this mean by more than 0.02 of 1%. We believe 0.1 of 1% to be the limit of error of this determination.

TABLE V

HEAT OF VAPORIZATION OF NITRIC OXIDE

Boiling point, 121.36°. Molecular weight, 30.008

Moles of NO evaporated	0.21677	0.21729	0.21711	0.21646	
AH, 760 mm., cal./mole	3292.8	3291.8	3293.8	3292.1	Av. 3292.6 ± 3.3

No other calorimetric values for the heat of vaporization of nitric oxide are to be found in the literature.

Vapor Pressures of Nitric Oxide.—The best recent determinations of the vapor pressures of solid and liquid nitric oxide are those of Henglein and Kruger[17] and of Goldschmidt.[18] Both claimed high accuracy for their values, yet there is comparatively wide disagreement between the two sets of data. Since we had very pure nitric oxide and since the calorimetric apparatus employed was likewise admirably suited to the accurate measurement of vapor pressures, it seemed desirable to make a redetermination of vapor pressures. The data were obtained by the procedure already used by Giauque, Johnston and Kelley[20] for oxygen and hydrogen. For each vapor pressure point the calorimeter, nearly full of the liquid or solid nitric oxide, was heated to the desired temperature and allowed to stand for nearly an hour to insure thermal equilibrium before the temperature and pressure were taken. To avoid distillation the surroundings were maintained at a temperature slightly above that of the calorimeter. Pressures were read with the aid of a standard meter scale and a Société Génévoise Cathetometer. Corrections for temperatures of mercury and scale and for meniscus height were applied as described in connection with the measurement of the amount of gas in a previous paper.[1] The measurements were obtained with a precision of 0.002 cm. The measurements for solid nitric oxide began at 94.62°K. and were all made with Preparation II. Those for the liquid were begun with Preparation II and carried to about 116°. An accident occurred which interrupted the measurements at this point and subsequently the measurements were repeated with Preparation III and extended to nearly 123°K. The triple point pressure was investigated with Preparations I, II and III in turn.

The results are tabulated in Table VI. In this table the first column gives the preparation number; the second, the observed temperature in degrees absolute; the third, the observed pressure in international centi-

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[20] Giauque, Johnston and Kelley, THIS JOURNAL, 49, 2367 (1927).

meters; the fourth, the temperature calculated by substituting the observed pressures in the vapor pressure equations which we have derived; the fifth, the pressure calculated by substituting the observed temperatures in our vapor pressure equations; the sixth, pressure observed minus pressure calculated; the seventh, temperature observed minus temperature calculated and the eighth, the physical state of the nitric oxide.

TABLE VI

THE VAPOR PRESSURE OF NITRIC OXIDE

Prepn.	T, °K., obs.	P, int. cm, obs.	T, calcd.	P, calcd.	ΔP, int. cm.	ΔT, °K.	Remarks
II	94.62	0.918	94.64	0.912	+0.006	−0.02	Solid
II	96.47	1.366	96.45	1.372	− .006	+ .02	Solid
II	98.77	2.227	98.76	2.230	− .003	+ .01	Solid
II	100.84	3.396	100.85	3.389	+ .007	− .01	Solid
II	102.92	5.082	102.93	5.075	+ .007	− .01	Solid
II	104.41	6.700	104.40	6.711	− .011	+ .01	Solid
II	106.68	10.101	106.67	10.121	− .020	+ .01	Solid
I	109.49	16.442					Triple point
II		16.440					Triple point
II		16.441					Triple point
III		16.442					Triple point
III		16.433					Triple point
III		16.432					Triple point
	Average	16.438 ± 0.004	109.49	16.438	0.000	0.00	Triple point
III	110.75	19.662	110.75	19.660	+0.002	0.00	Liquid
II	111.67	22.267	111.65	22.339	− .072	+ .02	Liquid
III	112.67	25.651	112.68	25.609	+ .042	− .01	Liquid
II	113.90	30.143	113.89	30.199	− .056	+ .01	Liquid
III	114.95	34.646	114.95	34.646	.000	.00	Liquid
II	116.18	40.604	116.19	40.571	+ .033	− .01	Liquid
III	117.28	46.588	117.28	46.584	+ .004	.00	Liquid
III	119.53	61.296	119.53	61.301	− .005	.00	Liquid
III	121.18	74.328	121.16	74.465	+ .063	+ .02	Liquid
III	122.93	90.990	122.93	90.990	.000	.00	Liquid

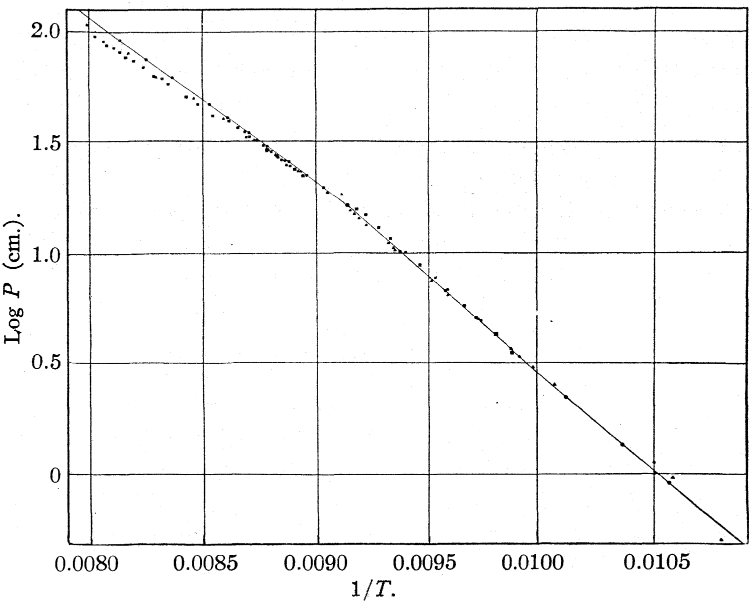
The data are represented by vapor pressure equations which take the form, for solid

$$\log_{10} p(\text{cm.}) = \frac{-867}{T} + 0.00076\,T + 9.05125$$

and for liquid

$$\log_{10} p(\text{cm.}) = \frac{-776}{T} - 0.002364\,T + 8.562128$$

As shown from the ΔT column of Table VI, the agreement between experimental values and the values given by these equations is exceptionally good. Almost without exception the experimental points fit these equations within the limits of the thermocouple readings. The results are shown graphically in Fig. 2, where log p is plotted against $1/T$. The nearly linear curves intersecting at the triple point represent the above two equations. Our experimental points are plotted in dark circles. For comparison the results of Henglein and Kruger are plotted in dark squares and those of Goldschmidt in dark triangles. The scale of the graph is really too insensitive to indicate the extent of the disagreement. Table VII shows a comparison of the smoothness of these data with those of Henglein and Kruger and of Goldschmidt, by comparing the mean deviations and the extreme deviations of each observer's data from the vapor pressure equations derived by the respective workers. The comparison is made over the same range of temperature for each set of data, a little above 90° to the boiling point. The first line lists the research, Line 2 the extremes of AT from the vapor pressure equation derived to fit and the third line the average deviation in degrees absolute.



●, This Research; □, Henglein and Kruger; ▲, Goldschmidt.

Fig. 2.—Vapor pressure of solid-liquid and liquid nitric oxide.

TABLE VII

DEVIATION OF EXPERIMENTAL DATA FROM THE EQUATIONS WHICH REPRESENT THEM

	Henglein and Kruger[17]	Goldschmidt[18]	This Research
Extremes of ΔT, °K.	\$0.30 to -0.30	$+0.30$ to -0.50	$+0.02$ to -0.02
Average AT, °K.	0.12	0.08	<0.01

Comparisons of triple point pressures are made in Table III, where the triple point temperatures were recorded. The present value is the mean of the six direct determinations recorded in Table VI and is consistent for three separate lots of nitric oxide. It is believed to be correct to within

0.004 cm. The triple point pressure of Henglein and Kruger was not determined from direct measurement but was calculated from their vapor pressure equations, and was likewise their triple point temperature. Goldschmidt's value was obtained from a single direct measurement.

In Table VIII are given the values for the boiling point of nitric oxide as determined by the vapor pressure measurements of various observers.

TABLE VIII

BOILING POINT OF NITRIC OXIDE

Observer	T, °K.	Observer	T, °K.
Olszewski[19]	119.5	Henglein and Kruger[17]	122.4
Ramsey and Travers[21]	123.2	Goldschmidt[18]	121.87
Adwentowski[S]	122.8	This Research	121.36 ± 0.05

Differences in temperature scales undoubtedly are a contributing factor to the vapor pressure differences found by various observers. This cannot account, however, for differences in the triple point pressure. It is believed that the difficulty of preparing nitric oxide in a high state of purity has been a prominent factor. It is a significant fact that the present measurements, which were carried out with very pure nitric oxide, lead to a lower value for the boiling point and to higher vapor pressures for the liquid than do other recent researches.

Purity of Nitric Oxide.—Measurements of heat capacity just below the melting point serve as a very sensitive test of impurity. Measurements were purposely made close to the melting point in order to make such a test. Insoluble impurities would not cause premelting but they could hardly be present under the circumstances of preparation and purification.

For the most probable case of pure solid in equilibrium with impure liquid, we have, assuming Raoult's law, the equation

$$\ln N_1 = \frac{-\Delta H}{R}\left(\frac{T_m - T}{T_m T}\right)$$

where N_1 refers to the mole fraction of nitric oxide, ΔH is its heat of fusion and T_m is the melting point. This equation gives us the mole fraction of nitric oxide in any liquid which may be formed by premelting at temperature T. The heat effect accompanying premelting will depend on $\Delta H \times$ (A" − A'), where A'' and A' refer, respectively, to the amounts of liquid nitric oxide at T'' and T'. The heat effect is obtained by taking the difference between the observed input from T' to T'' and that which would be calculated from an assumed curve such as is indicated by the dotted line in Pig. 1. We now have sufficient information to solve for the number of moles of impurity, which must be a constant. The results are given in Table IX. The amount of impurity is expressed in mole percentage rather than in mole fraction.

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[21] This value was quoted in Ref. 17.

TABLE IX

MOLE PERCENTAGE OF IMPURITY IN NITRIC OXIDE

Preparation III

T'	T''	Heat of pre-melting calories	N'_1	N''_1	Impurity. mole per cent.
104.71	108.59	0.171	0.8956	0.9795	0.00079
107.63	109.15	.365	.9580	.9922	.00064
From melting point change of Preparation II					.0004

At the bottom of the table a value obtained from the less sensitive method of melting point rise is included. In determining the melting point of Preparation II, a measurement was purposely made with only about 3% melted in order to make as severe a test as possible. From the data recorded in Table II the amount of impurity was evaluated. It should be a reasonable conclusion that the nitric oxide contained less than 0.001 mole per cent. of impurity.

Some Physical Characteristics of Liquid and Solid Nitric Oxide.—The assignment of physical characteristics to solid and liquid nitric oxide has been influenced by the recognized impurity of the substance examined by those who have reported. Adwentowski[6] describes the liquid as colorless in thin layers and light blue in thick layers and ascribes the blue color to the presence of nitrogen trioxide impurity. Henglein and Kruger refer to the liquid as pale blue, resembling liquid oxygen. Nearly all writers refer to the solid as a "snow white" solid and this description is accepted without question in books of reference. In this investigation, we dealt with large quantities of solid and liquid in a high state of purity. The liquid was blue in color, a much darker and more brilliant blue than liquid oxygen with which we had every opportunity of comparison since in the course of the oxygen investigation liquid oxygen was collected in some of the same collecting bulbs used for the nitric oxide. If this blue were due to the small traces of impurity present a marked change in color intensity should have been observed in the course of the purification; no such change was observed. The appearance of the solid depended on our method of freezing it. If collected as a sublimate on the walls of the collecting bulb it had the appearance of a white frost, the "snow white" solid of the literature, but if this same sublimate were allowed to warm to the melting point, it was converted into a clear blue ice. Freezing the liquid always produced this clear blue ice, resembling in shade and intensity the coloration of the liquid. If a glass bulb filled with this clear blue solid was suddenly immersed in liquid air the nitric oxide became filled with innumerable cracks which made the solid appear white and opaque, although blue splotches of varying shades of intensity remained in places where the cracking was not as complete. Further investigation convinced us that the white appearance of the solid secured under certain conditions of freezing is a purely superficial effect caused by the crystalline state of aggregation throughout the mass and that the true color of the solid is blue. Thus both liquid and solid are blue in color.

Entropy from Heat Capacity Data.—The entropy of nitric oxide gas at the boiling point of the liquid was calculated from the calorimetric measurements by integration of the heat capacity data with respect to the logarithm of temperature. A summary of the entropy calculation is given in Table X. The extrapolation below 14.35°K. was carried out by means of a Debye function with a $\beta\nu = 119$.

TABLE X

ENTROPY OF NITRIC OXIDE FROM HEAT CAPACITY DATA

	Cal. per degree per mole
0 to 14.35°K. (extrapolated)	0.27
14.35 to 109.49° (graphical)	8.79
Fusion 549.5/109.49	5.02
109.49 to 121.36 (graphical)	1.73
Vaporization 3292.6/121.36	27.13
Entropy of nitric oxide gas at the boiling point	42.94 ± 0.1 E. U.

This value is for the actual gas. For the purpose of later comparison with the entropy derived from band spectra, it is necessary to have the entropy of the hypothetical perfect gas. Assuming Berthelot's equation of state, a correction of 0.09 cal./deg. per mole results, leading to a value of 43.03 for the entropy of nitric oxide gas in the hypothetical ideal state at 121.36°K.

The entropy has also been calculated with the assistance of the thermodynamic equation $dP/dT = \Delta S/\Delta V$ and our vapor pressure data for both solid and liquid. The entropy of vaporization was calculated at the triple point temperature in each case, making use of Berthelot's equation in order to correct for gas imperfection. The entropy of solid or liquid at the melting point may be obtained from Table X. In order to obtain the entropy change in heating the gas from the triple point to the boiling point, we assumed that C_p was 7/2 R and corrected for the error in this assumption by an approximate calculation of the entropy change accompanying the changing distribution of the $^2P_1$ and $^2P_2$ states. From the solid $S_{NO} = 43.3$ E. U., and from the liquid $S_{NO} = 43.0$ E. U., each calculated to the temperature of the boiling point, as compared to 43.0 E. U. obtained from the calorimetric measurements. This agreement is all that could be expected of the vapor pressure calculations and we give these two calculations no weight as compared to the calorimetric data.

The heat of vaporization at the boiling point has also been calculated from the vapor pressure data for liquid nitric oxide, again using Berthelot's equation to represent gas imperfection. The value obtained for $\Delta H_{121.36°K.}$ is 3316 cal. per mole as compared with the more accurate calorimetric value 3293. Similar calculations by Henglein and Kruger[17] and by Goldschmidt[18] from their respective vapor pressure data lead to the values 3023 and 3199.

Spectroscopic Interpretation of Nitric Oxide.—Jenkins, Barton and Mulliken[2] have obtained measurements of the fine structure of the β-bands of nitric oxide and have made an analysis of the lines in keeping with Hund's theory[22] of molecular electronic states and with recent developments in the interpretation of band spectra as reviewed and extended in a number of papers by Mulliken.[23] The classification of the lines revealed the presence of two distinct band systems. The application of the combination principle taken in conjunction with the positions of missing lines in the various branches led to the assignment of proper j values and to the proper term formulation for the initial and final electronic levels of the two band systems. The term formulations show that the two band systems originate from respective transitions from a double initial electronic level to a double final electronic level $({}^2P_1 \longrightarrow {}^2P_1)$ $({}^2P_2 \longrightarrow {}^2P_2)$. In the lower states the ${}^2P_2$ level has a higher energy than the ${}^2P_1$ level. The separation is 124.4 cm.$^{-1}$. The magnitude of separation was obtained from the analysis by Frl. Guillery[24] of the y-bands of nitric oxide, which are likewise a double band system, having the same final double electronic state as do the β-bands. From the fact that both β- and y-systems appear in the absorption spectra of nitric oxide,[25,26] it is evident that this lower double level is the normal state of the nitric oxide molecule.

A physical concept of alignment and quantization of momenta within the molecule is desirable to make clear the assignment of j values and of *a priori* probabilities necessary in the application of the spectroscopic data to the calculation of entropy. Hund has shown that molecules containing resultant electronic angular momentum and electron spin will have their rotation states defined by the three vectors: σ_k, the component of electronic angular momentum directed along the figure axis of the molecule; S, the electron spin and m, the rotational momentum of the molecule. Any component of electronic angular momentum other than that directed along the axis of the molecule is assumed to be without effect on the molecular motion due to the rapid procession. This latter assumption is, of course, in agreement with the observed facts of band spectra.

For nitric oxide $s = {}^1/_2$ and $\sigma_k = 1$. Neglecting at first the molecular rotation, the spin s sets itself either with or against σ_k, thus leading to the

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[22] Hund, *Z. Physik*, 36, 657 (1926).

[23] Mulliken, *Phys. Rev.*, **28**, 482 (1926); **28**, 1202 (1926); 29, 391, 637 (1927); 30, 138, 785 (1927).

[24] Guillery, *Z. Physik*, 42, 121 (1927).

[25] Liepson, *Astrophys. J.*, 63, **73** (1926).

[26] Sponer and Hopfield, *Phys. Rev.*, **27**, 640 (1926).

doublet state referred to above. In the $^2P_1$ state s opposes, σ_k and in the $^2P_2$ state, s is with σ_k. When the rotation of the molecule is taken into account, Hund has shown that for increasing values of m, the influence of σ_k is relatively weakened as compared to that of m. The spin, s, gradually breaks away from its close coupling with σ_k and, in the limit, aligns itself either directly with or directly against the vector j_k (j_k is the vector sum of σ_k and m).

The vector sum of σ_k, s and m leads to the single vector j, which represents the total angular momentum of the molecule. Under all circumstances j is rigidly quantized. It is significant to observe in this connection that in meeting the conditions of quantization in the several instances referred to above, m itself is not quantized and, except for the special case of a molecule with $\sigma_k = 0$, cannot be quantized. Indeed, when a σ_k is present, the various m states not only differ by non-integral amounts of momentum but even the increments in momentum change in passing from one pair of rotation states to the next. The various rotational energy states are thus correlated with quantized terms which are j terms. Particular attention is called to this point because in the past m rather than j has frequently been regarded as the significant quantity in applying band spectra to the heat capacity and the entropy calculations.

It may be seen from the geometry of the model built up in the paragraphs above that j may be equal to the vector sum of σ_k and s (for $m = 0$) but never less. Hence the $^2P_1$ state has associated with it j values $= {}^1/_2$, ${}^3/_2$, ${}^5/_2 \ldots$, while the $^2P_2$ state can include no value $j = {}^1/_2$ but has associated with it the j values $= {}^3/_2$, ${}^5/_2$.

In fixing the *a priori* probability of a particular state of the molecule j, and not m, is the significant quantity to be considered. The *a priori* probability of a particular state is given by the wave mechanics as $(2j + 1)$.

The above was shown very definitely by the fine line structure photographed by Jenkins, Barton and Mulliken and by the intensity measurements of the same authors.[27] The j values used by the latter and by Mulliken[23] are larger by ${}^1/_2$ unit than the wave mechanics j values, hut as they used $2j$ as the *a priori* probability, the same results are attained. In the tables the wave mechanics values for the vibrational quantum number n are used to replace the values given in their tables, which were one-half unit lower.

One further important consequence of the theory of Hund must be considered. From the equations of Hund it follows that for a molecule like nitric oxide, possessing a component σ_k, associated with every value of j there should be not two (corresponding to $^2P_1$ and $^2P_2$ states) but four states of the molecule of equal *a priori* probability. This should lead to four series of bands provided the energies corresponding to the states of

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[27] Jenkins, Barton and Mulliken, Phys. *Rev.*, 30, 175 (1927).

the last two members of the multiplet were sufficiently different from the first two. Jenkins, Barton and Mulliken did find a fine scale doubling in the lines of the $^2P_1$ band series and, where resolution was sufficiently great for intensity measurements, the intensity relations corresponded to the equal *a priori* probability assignment. No such fine scale doubling was found in the lines of the $^2P_2$ band system but it is probable that double states of almost equal separation existed in the initial $^2P_2$ level as well as in the final level so that the doubling could not be observed in the spectra. This type of superfine doubling is well recognized in other spectra of molecules possessing a component σ_k and is referred to as a-type doubling. Mulliken[23] refers to the energy levels that give rise to the members of the doublets as A and B sub-levels.

The Entropy Calculated from the Spectroscopic Data.—The entropy of nitric oxide gas has been calculated for a temperature of 121.36°K. and also for 298.1°K. To obtain that portion of the entropy resulting from the translational energies of the molecules, we have employed the Sackur equation for the entropy of a monatomic gas

$$S = \frac{3}{2} R \ln M + \frac{3}{2} R \ln T + R \ln V - 11.06$$

M is the molecular weight, T the absolute temperature, V the molal volume in *cc.* and R is the gas constant taken as 1.9869 cal./deg. per mole.

To obtain that portion of the entropy contributed by the degrees of freedom other than translation, we have used the summation method[28,1]

$$S_{E+R+V} = R \ln \Sigma_{e,n,m} p_{e,n,m} e^{-\epsilon_{e,n,m}/kT} + \frac{1}{kT} \frac{\Sigma_{e,n,m} p_{e,n,m} \epsilon_{e,n,m} e^{-\epsilon_{e,n,m}/kT}}{\Sigma_{e,n,m} p_{e,n,m} e^{-\epsilon_{e,n,m}/kT}}$$

$\epsilon_{e,n,m}$ is the energy of a certain state with respect to electronic configuration, molecular vibration and molecular rotation, respectively; $p_{e,n,m}$ is the corresponding *a priori* probability, *e* the base of the natural logarithms and k the gas constant per molecule.

The above equation has been used in conjunction with the data and spectroscopic interpretation of Jenkins, Barton and Mulliken[2] as outlined above.

In carrying out the required summations in the calculations which follow, it has been convenient to make the summations as though a-type doubling did not exist. Then each sum was doubled before incorporating it in the entropy equation. This method is justified since the energy differences of A and B substates are so small that the same energy may be assigned for each state (the spectroscopic measurements were taken at the middle of the double lines) and the total energy and total numbers in both A and B states will be double that in either one.

Table XI shows the values obtained for the significant sums which appear in the entropy equation for T = 121.36°K.

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[28] Giauque and Wiebe, THIS JOURNAL, 50, 101 (1928).

TABLE XI

SUMS IN THE ENTROPY EQUATION FOR NITRIC OXIDE

$n = 1/2 \quad T = 121.36°K.$

e	$\Sigma_m p_m e^{-\epsilon_m/kT}$	$1/kT\ \Sigma_m \epsilon_m p_m e^{-\epsilon_m/kT}$
$^2P_1$	51.364	50.529
$^2P_2$	11 053	27.553
$\Sigma_{e,n,m}$	62.417	78 082
Doubled for u-type doubling	124.834	156 164

It is interesting to note that the distribution of molecules between the $^2P_1$ and $^2P_2$ states at the boiling point of nitric oxide is 82.29% of $^2P_1$ molecules to 17.71% of $^2P_2$ molecules. This unequal distribution is a result of the 124 odd wave numbers difference in energy between the two forms of coupling. The fraction of molecules in higher vibration states has been calculated and found to be inappreciable for this temperature. Putting the above sums into the entropy equation

$$S_{E+R+V} = 12.08 \text{ E. U.}$$

Combining this value with the 31.67 entropy units contributed by the translation of the molecules, the entropy of the hypothetical perfect nitric oxide gas at one atmosphere pressure and 121.36°K. has the value 43.75 calories per degree per mole.

The result of a similar calculation for a temperature of 298.1°K. is given in Table XII.

TABLE XII

SUMS IN THE ENTROPY EQUATION FOR NITRIC OXIDE

$T = 298.1°K.$

e	n	$\Sigma_m p_m e^{-\epsilon_m/kT}$	$1/kT\ \Sigma_m \epsilon_m p_m e^{-\epsilon_m/kT}$
	1/2	124.864	124.107
$^2P_1$	3/2	0.917	5.419
$^2P_1$	5/2	.007	0.078
	7/2	.000	.001
$^2P_2$	1/2	65.721	105 804
$^2P_2$	3/2	0.480	3.131
$^2P_2$	5/2	.004	0 043
$^2P_2$	7/2	.000	.001
$\Sigma_{e,n,m}$		191.993	238 584
Doubled for u-type doubling		383.986	477.168

This leads to the value $S_{298\cdot1} = 50.43$ E. U.

There is one further type of multiplicity which makes a contribution to the absolute entropy of nitric oxide which we have not considered in the above calculation, since it would be expected to affect the spectroscopic and $\int_0^T C_p \mathrm{d}\ln T$ calculations equally. This arises from the one unit of spin associated with the nitrogen nucleus and contributes R ln **3** entropy units to the value of the absolute entropy.

Comparison of Entropy Values.—The theoretical and experimental values of the entropy are compared in Table XIII.

TABLE XIII

COMPARISON OF SPECTROSCOPIC AND THIRD LAW VALUES OF THE ENTROPY OF NITRIC OXIDE

T, °K.	121.36	298.1
Entropy from spect. data, cal./deg./mole	43.75	50.43
$^{T}C_p\mathrm{d}\ln T$ Actual gas	42.94 ± 0.1	...
$^{T}C_p\mathrm{d}\ln T$ Corr. to ideal state	43.0	...

It is clear that the experimental value is in definite disagreement with that calculated from the spectroscopic data.

It appears significant that the entropy obtained from the calorimetric measurements is lower than that obtained by the spectroscopic method by almost exactly $^1/_2$ R ln 2. This can be explained if solid nitric oxide is a solution of two polymerized isomers in equal amount. Liquid nitric oxide is known to be highly associated into N_2O_2 molecules and it appears reasonable that this effect would persist in the solid. Solid isomers would result if, in the process of association, more than one type of pairing could occur between molecules which retained some of the electronic differences they possessed in the gaseous state, such as the differences responsible for a-type doubling. An equimolal mixture of two such isomers of small energy difference would possess an entropy in excess of that obtained from the heat capacity measurements by an amount equal to R ln 2 entropy units per mole of polymerized molecules. This is equivalent to $^1/_2$ R ln 2 entropy units per stoichiometrical mole. The solid nitric oxide would thus appear to go to the absolute zero with 0.69 entropy units per mole still present. The discrepancy between the entropy values obtained from calorimetric and from spectroscopic data, respectively, is 0.72 entropy unit.

We do not regard this as a contradiction of the third law of thermodynamics, although it has an important bearing on the application of that law to thermodynamic problems. In conformity with views expressed in previous papers,[4,5] it is believed that if nitric oxide could be cooled to the absolute zero and be allowed to reach true equilibrium, a transformation would occur to a single species of molecule having zero entropy. This transformation would result from the energy difference which, though small, must exist between the isomeric forms. Expressed in other terms, we believe that if measurements of the heat capacity of nitric oxide could be carried to the absolute zero under equilibrium conditions, the results would fall on a curve which would show a maximum, close to the absolute zero, which would just account for the observed entropy difference.

We wish to thank Mr. J. O. Clayton for assistance in the experimental work and in the calculations. We also wish to thank Professor R. T. Birge for many discussions of the spectroscopic data and their interpretation.

Summary

Nitric oxide containing less than 0.001 mole per cent. of impurity has been prepared. Both solid and liquid were found to be blue in color. The accepted opinion that solid nitric oxide is colorless is apparently based on observations on material in a fine state of subdivision. Under such conditions it was found to have this appearance.

The heat capacities of solid nitric oxide and of the liquid have been measured from 14°K. to the boiling point. From the boiling point to 35°K. the smooth curve through the points is believed to be accurate to within 0.2 of 1%; below this temperature there is a gradual decrease in accuracy. At 20°K. the results are believed to be reliable to 0.7 of 1%, and at 14°K. to 2 or 3%.

The melting point was found to be 105.49 ± 0.05°K.; the boiling point 121.36 ± 0.05°K.

Calorimetric determinations of the heat of fusion and of the heat of vaporization were made. These were found to be 549.5 ± 1.0 and 3292.6 ± 3 calories per mole, respectively.

The vapor pressures of solid and liquid nitric oxide have been measured between 93 and 123°K.

The entropy of nitric oxide gas at 121.36°K. and one atmosphere was calculated from the above data and the third law of thermodynamics, and found to be 42.94 ± 0.1 calories per degree per mole. With the aid of Berthelot's equation of state this value was corrected to the ideal state, the correction being +0.09 calorie per degree per mole. When compared to the value calculated by the accurate summation method from the molecular spectrum of nitric oxide gas, the value obtained from the heat capacity measurements proved to be too low to the extent of 0.72 calorie per degree per mole. This is not taken as a contradiction of the third law of thermodynamics but is believed to arise from the presence of equimolal amounts of two forms of N_2O_2 in the solid state. This situation, which would lead to a difference of $^1/_2$ R ln 2 or 0.69 E. U. in comparison with the experimental amount of 0.72 ± 0.1 E. U., might be expected from the selective combination of molecules in the A and B substates resulting from the axial component of momentum of the nitric oxide molecule.

The two substates of nitric oxide are practically identical in energy and it is not surprising that the heat capacity measurements do not extend, and possibly cannot be extended, to sufficiently low temperatures to make the thermodynamic equilibrium produce a perfectly ordered crystalline state. This is a matter of considerable practical importance since it indicates that the correct use of the third law of thermodynamics will occasionally require information in addition to that supplied by heat capacity measurements.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

BASIC CATALYSIS IN THE DECOMPOSITION OF DIACETONE ALCOHOL

BY C. CLEMENT FRENCH

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Introduction

In recent papers Åkerlöf[1] has presented the results of a careful study of the catalytic decomposition of diacetone alcohol by strong bases in aqueous solution, with and without added salt. This decomposition takes place according to the equation $C_6H_{12}O_2 \longrightarrow 2(CH_3)_2CO$. An attempt was made to explain the salt effect as a function of the individual ion activity of the hydroxyl ion. In the aqueous solutions of potassium, sodium and lithium hydroxides, in the absence of added salts, a direct proportionality was found between the activity of the hydroxide and the velocity of the reaction. As it appeared that this relation failed to remain valid below an hydroxide concentration of 0.1 M, measurements of the velocity in solutions of sodium and potassium hydroxides below this concentration have been carried out in order to determine what relation exists in the more dilute solutions.

In the study of the effect of salts on the rate of this decomposition, Åkerlöf used a 0.1 *M* alkali solution, with the concentration of added salt varying from 0 to 5 M at 0.5 M intervals. In connection with the investigation of the velocity in solutions of base more dilute than 0.1 M, it was thought advisable to examine the effect of a few salts in concentrations up to 1 M. The purpose of these experiments in the presence of neutral salts was to determine the salt effect in the region where the Bronsted theory predicts a linear salt effect and to determine whether the magnitude of the salt effect changes with change in the concentration of the catalyst.

The study by Åkerlöf[2] of the decomposition of diacetone alcohol by some amine bases suggested the possibility that this decomposition might be catalyzed by negative ions other than the hydroxyl ion. To test this possibility, a few experiments were made in phenol–sodium phenolate buffers.

Experimental Method

The apparatus, as well as the experimental method used, was the same as that described by Åkerlöf in the papers mentioned above and does not require further discussion. Since the half time of all measurements reported here is greater than twenty minutes, there was always sufficient time available for the reacting solution to come to thermal equilibrium in

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[1] Åkerlöf, THIS JOURNAL, 48, 3046 (1926); *ibid.*, 49, 2955 (1927).

[2] Åkerlöf, *ibid.*, 50, 733 (1928).

the thermostat before readings were begun. Consequently, in only a few cases were values of k obtained showing a drift of more than 2%. In these cases the measurements were repeated with new solutions.

Experimental Results and Discussion

A. Aqueous Solutions of Potassium and Sodium Hydroxides.—A summary of the measurements with these solutions is given in Table I. All concentrations are expressed in molality or moles of solute per 1000 g. of water. The diacetone alcohol was present in a concentration of about 0.15 M. Experiments were reproducible to within 2%. The velocity constants are expressed with the minute as the unit of time. All experiments were carried out at 25°.

TABLE I

DECOMPOSITION VELOCITY OF DIACETONE ALCOHOL IN SOLUTIONS OF POTASSIUM AND SODIUM HYDROXIDES

	Potassium hydroxide		Sodium hydroxide	
Molality, M	0.434 k X 10^4	0.434 k/M	0.434 k X 10^4	0.434 k/M
0.005	10.1	0.202	...	..
.0100	20.3	.203	20.1	0.201
.0200	40.8	.204	40.4	.202
.0400	83.3	.208	82.7	.206
.0500	105.4	.211	105.1	.210
.0655	...	..	134.0	.204
.0700	142.9	.204		
.0755	...	..	156.4	.202
.0800	164.1	.205	..	..
.0850	173.9	.204	...	..
.100	208.0	.208	206.0	.205
	(211.0)[a]	..	(208.0)[a]	..
	Average	.205	Average	.204

[a] These values are taken from the paper of Åkerlöf, THIS JOURNAL, 49, 2960 (1927), Table IV and show the agreement obtained.

In Fig. 1, 0.434 k X 10^4, the observed velocity constant, has been plotted against the alkali hydroxide concentration. The figure shows that up to 0.1 M base, the velocity is almost directly proportional to the hydroxide concentration. Also, from Table I it can be seen that the values of 0.434 k/M deviate from the average value within the experimental error, and give a satisfactorily constant value for 0.434 k/M.

Åkerlöf[3] found that a close relationship existed between the activity of the hydroxide and the reaction velocity in solutions of sodium and potassium hydroxides above 0.2 M. For the concentration range from 0.2 to 2.0 M, the expression $\gamma M/K$, where γ = the activity coefficient of the hydroxide, M the molality of the hydroxide and K the observed velocity constant, was a constant within the experimental error. A similar calculation has been carried out here to show how widely this expression deviates

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[3] Åkerlöf, THIS JOURNAL, 49, 2962 (1927).

from a constant value when the molality of the alkali hydroxide is 0.1 M or less. The results are shown in Table II. The activity coefficients were calculated from the equation

$$\log \gamma_{\mathrm{MeOH}} = \frac{-0.354\sqrt{2m}}{1 + A\sqrt{2m}} + B2m - \log\left(1 + \frac{36m}{1000}\right)$$

where γ is the activity coefficient, A and B are empirical constants and m is the molal concentration of the base. The values of ***A*** and B are given in Table II and are those calculated by Warned and Åkerlöf.[4]

For values of m above 0.2, the values of $\gamma M/0.434\ k \times 10^2$ for both sodium and potassium hydroxides remain constant.

The statement made by Harned and Åkerlöf[5] that this relation was probably not valid in the concentration range shown here is confirmed by the results in the table above. Therefore, it seems there is no doubt that in aqueous solutions of sodium and potassium hydroxides, below 0.2 M concentration, the decomposition velocity of diacetone alcohol is determined by the concentration of the hydroxide present and not by its activity. It is in this range of concentration that the activity of the alkali hydroxides is changing most rapidly, so that an agreement of the velocity with the change in activity of the hydroxide rather than with its concentration would show a marked deviation from the straight line relation in Fig. 1.

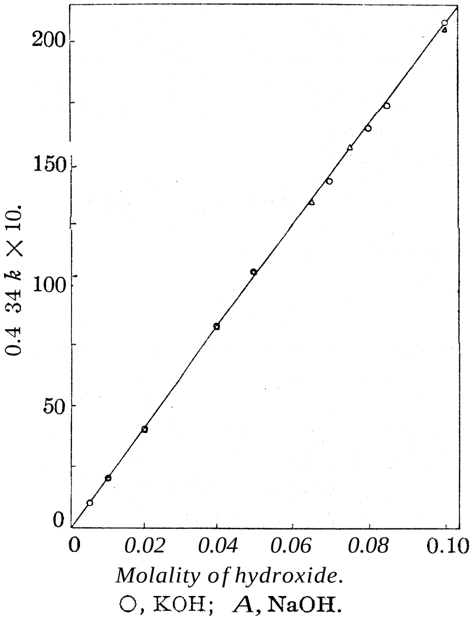

Fig. 1.—Effect *of hydroxyl ion on* the decom*position of diacetone alcohol.*

According to the Bronsted theory, the velocity of a reaction of this type would be expressed by the equation

$$v = kc_{\mathrm{A}}c_{\mathrm{OH}^-}\frac{f_{\mathrm{A}}f_{\mathrm{OH}^-}}{f_{(\mathrm{A,\,OH})^-}}$$

which in dilute solution would reduce to the simple equation

$$v = kc_{\mathrm{A}}c_{\mathrm{OH}^-}$$

since $f_{\mathrm{A}}f_{\mathrm{OH}^-}/f_{(\mathrm{A,\,OH})^-}$ will equal unity. In the concentration range considered here, this simple equation appears to express correctly the decomposition rate.

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[4] *Harned and* Åkerlöf, *Physik. Z., 27,411 (1926).*

[5] *Harned and* Åkerlöf, *Trans. Faraday Soc., No. 90, 24, Part* 11, **p.** *676 (1928).*

Table II

Relation between the Activity of the Hydroxide Present and the Velocity of Decomposition of Diacetone Alcohol

Molality of base, M	Potassium hydroxide γ	Potassium hydroxide $\frac{\gamma M}{0.434} \times 10^2$	Sodium hydroxide γ	Sodium hydroxide $\frac{\gamma M}{0.434\,k} \times 10^2$
0.005	0.928	463	..	...
.0100	.903	444	0.902	448
.0200	.873	427	.869	430
.0400	.836	401	.830	401
.0500	.823	394	.815	388
.0655	..	...	.798	391
.0700	.803	390	..	...
.0775	..	...	.786	390
.0800	.796	388	..	...
.0850	.792	386	..	...
.100	.783	376	.767	374
.200	.745	371	.716	366
$A = 0.777$. $B = 0.0632$			$A = 0.660$. $B = 0.050$	

As will be shown later, the spontaneous water reaction is entirely negligible here.

Table III

Decomposition of Diacetone Alcohol in 0.050 M Sodium Hydroxide–Sodium Salt Solutions

Molality of added salt	Total equiv. salt concn.	$0.434\,k \times 10^4$	$0.434\,k_2$
Sodium Chloride			
0	0.050	105.1	0.210
0.100	.150	101.7	.203
.200	.250	98.1	.196
.400	.450	91.9	.184
.600	.650	86.5	.173
.800	.850	81.8	.164
1.00	1.050	77.2	.154
Sodium Bromide			
0.100	0.150	99.9	0.200
.200	.250	95.0	.190
.400	.450	88.6	.177
.600	.650	82.3	.165
.800	.850	76.9	.154
1.00	1.050	71.2	.142
Sodium Iodide			
0.100	0.150	98.6	0.197
.200	.250	92.6	.185
.400	.450	85.0	.170
.600	.650	78.2	.156
.800	.850	72.1	.144
1.00	1.050	66.0	.132

Table IV

Decomposition of Diacetone Alcohol in 0.050 M Potassium Hydroxide–Potassium Salt Solutions

Molality of added salt	Total equiv. salt concn.	$0.434\,k \times 10^4$	$0.434\,k_2$
Potassium Chloride			
0	0.050	105.4	0.211
0.100	.150	102.0	.204
.200	.250	98.5	.197
.400	.450	93.0	.186
.600	.650	89.3	.179
.800	.850	86.4	.173
1.00	1.050	84.2	.168
Potassium Bromide			
0.100	0.150	100.3	0.201
.200	.250	95.5	.191
.400	.450	88.7	.177
.600	.650	84.2	.168
.800	.850	81.1	.162
1.00	1.050	77.2	.154
Potassium Iodide			
0.100	0.150	98.5	0.197
.200	.250	92.5	.185
.400	.450	85.0	.170
.600	.650	78.8	.158
.800	.850	74.2	.148
1.00	1.050	69.8	.140

B. Alkali Hydroxide-Alkali Salt Solutions.—These experiments were all carried out with an alkali hydroxide concentration of 0.05 M and with the added salt concentration varying from zero to one molal. Concentrations are all expressed in molality. All solutions were made up by weighing in a known quantity of standard alkali solution, then adding a sufficient weight of water to make the solution 0.05 M. To this solution was added the calculated weight of dried salt. Table III summarizes the results for the sodium salts in the presence of sodium hydroxide and Table IV those for the potassium hydroxide–potassium salt solutions. The velocity constants have been calculated with the minute as the unit of time. The temperature of all experiments was 25°.

The total equivalent salt concentration in Col. 3 is the sum of the molality of the base and the molality of the added salt.

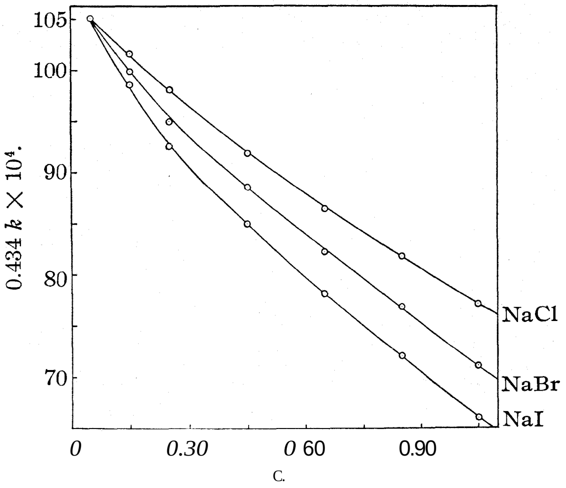


Fig. 2.—Effect of sodium salts on the decomposition of diacetone alcohol, c = $m_{\text{base}} + m_{\text{salt}}$.

The variation of the observed velocity constant, 0.434 k, with the total electrolyte concentration has been plotted in Fig. 2 for the sodium hydroxide–sodium salt solutions and in Fig. 3 for the potassium hydroxide–potassium salt solutions.

The fourth column in Tables II and III gives the observed velocity constant and the fifth column shows this constant divided by the concentration of hydroxyl ion, *i. e.*

$$k_2 = \frac{k_{\text{observed}}}{\text{molality of base}}$$

k_2 is then the molal velocity constant for the diacetone alcohol decomposition. In Fig. 4 0.434 k_2 is plotted against total electrolyte concentration (molality of base + molality of added salt) for the sodium hydroxide–sodium salt solutions and for the potassium hydroxide–potassium salt solutions, up to a total electrolyte concentration of 0.25 M. The salt effects of the base and of the added salt are taken as equal in the first approximation. The extent to which this approximation is incorrect may be judged from Fig. 4. Straight lines have been drawn through the various points at total electrolyte concentrations of 0.15 and 0.25 M, in such a way that all of these lines would meet at a point at zero electrolyte concentration. The two points at electrolyte concentration of 0.05 M represent the values for the bases in absence of added salt. The extent to which these points fail to lie on the various lines represents the error caused by assuming that the salt effect of the base and of the added salt will be equal. The smaller the concentration of the base in the total electrolyte concentration, the smaller will be the error introduced by this assumption, because the point on the plot for the base without added salt will be nearer the point of convergence of the various lines.

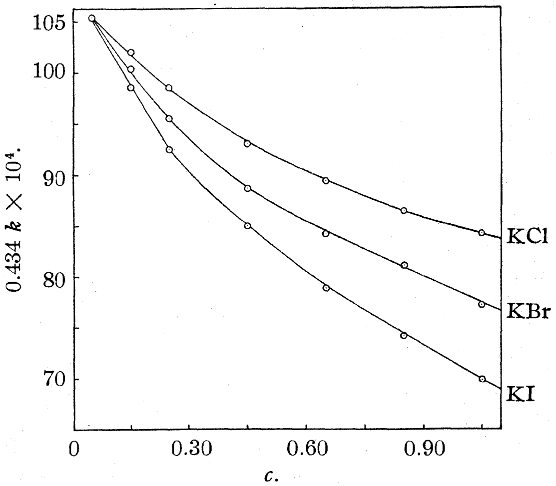


Fig. 3.—Effect of potassium salts on the decomposition of diacetone alcohol, $c = m_{\text{base}} + m_{\text{salt}}$.

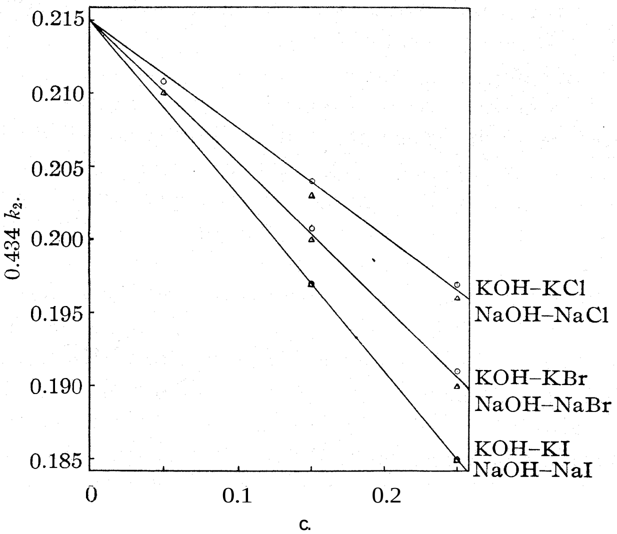
Above a total electrolyte concentration of 0.25 M the linear relationship which is found to exist in all six cases up to that concentration fails. For the concentration range below that value, the catalytic constant for diacetone alcohol in the various salt solutions may be represented by the following equations, where m is the total electrolyte concentration.

NaOH–NaCl, KOH–KCl $0.434\ k_2 = 0.215 - 0.074m$
NaOH–NaBr, KOH–KBr $0.434\ k_2 = 0.215 - 0.10m$
NaOH–NaI, KOH–KI $0.434\ k_2 = 0.215 - 0.12m$

From the above equations it is seen that the primary salt effect varies from about 3% for alkali chlorides to about 5.5% for alkali iodides.

Within the experimental error the equations for 0.434 k_2 depend upon the anion only.

In a consideration of the primary salt effect on the decomposition of nitrosotriacetone-amine, Kilpatrick[6] concluded that when the concentrations of the amine and of the salt were kept constant, and the hydroxyl ion concentration was varied, the salt effect was greater the lower the concentration of the hydroxyl ion. It is possible to test that conclusion for the diacetone alcohol reaction by a comparison of the results obtained here in 0.05 molal alkali solution, for given concentrations of added salts, with those obtained by Åkerlöf[7] for the same concentrations of added salts, but at 0.1 M alkali concentration. Table V contains such a comparison at added salt concentrations of 0.5 and 1 M.



○, KOH–KX; △, NaOH–NaX.

Fig. 4.—Variation of molal velocity constant with total electrolyte concentration, $c = m_{\text{base}} + m_{\text{salt}}$.

The values in Cols. 2 and 3 of Table V represent the percentage decrease in velocity at the salt concentrations indicated, referred to the velocity in the base alone at the concentrations of base shown for the two columns.

The suggestion of Kilpatrick regarding nitrosotriacetone-amine, mentioned above, does not appear to hold for this reaction. The differences between the percentage decreases for the same concentration of added salt in the different concentrations of base are no greater than would be

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[6] Kilpatrick, THIS JOURNAL, 48, 2091 (1926).

[7] Åkerlöf, *ibid.*, 48, 3051 (1926), Tables II and III.

TABLE V

COMPARISON OF SALT EFFECTS ON DECOMPOSITION OF DIACETONE ALCOHOL AT DIFFERENT HYDROXYL ION CONCENTRATIONS

Molality of added salt	Percentage salt effect in 0.1 M base	Percentage salt effect in 0.05 M base	Molality of added salt	Percentage salt effect in 0.1 M base	Percentage salt effect in 0.05 M base
0.5 M NaCl	18.3	15.1	0.5 M KCl	13.3	13.5
1.0 M NaCl	28.4	26.5	1.0 M KCl	21.3	20.2
0.5 M NaBr	20.6	18.7	0.5 M KBr	15.6	16.8
1.0 M NaBr	31.2	32.2	1.0 M KBr	25.1	26.7
0.5 M NaI	24.5	21.7	0.5 M KI	20.4	22.2
1.0 M NaI	37.5	37.2	1.0 M KI	33.2	33.8

introduced by the experimental error of the original velocity constant determinations. While in solutions of a lower hydroxyl ion concentration such a difference might be noticeable, it does not appear to be true where the hydroxide concentration is as high as 0.05 M or more.

C. Phenol-Sodium Phenolate Buffer Solutions.—Bronsted[8] defines a base as a substance which can take up hydrogen ions. Since the phenolate ion combines with a hydrogen ion to form phenol, it is a base by this definition, and a comparatively strong base since phenol is a weak acid. Consequently, it might be expected that the phenolate ion would decompose diacetone alcohol and an attempt was made to determine whether such was the case. Three buffer solutions were made up of phenol and sodium phenolate with the following concentrations: No. 1, 0.2 N sodium phenolate and 0.2 N phenol; No. 2, 0.15 N sodium phenolate, 0.05 N sodium chloride, 0.15 N phenol; No. **3,** 0.1 N sodium phenolate, 0.1 N sodium chloride, 0.1 N phenol. All three had a total electrolyte concentration of 0.2 N and a 1:1 ratio of phenol to sodium phenolate. The results are tabulated in Table VI.

TABLE VI

DECOMPOSITION OF DIACETONE ALCOHOL IN PHENOL-SODIUM PHENOLATE BUFFER SOLUTIONS

Solution no.	1	2	3
$0.434\ k_{\text{observed}}$	2.06×10^{-5}	2.02×10^{-5}	2.00×10^{-5}

The apparatus used was not designed to measure accurately very slow reactions, and for reactions such as those recorded above, with half times in excess of twenty-one days, an experimentally observed infinity value could be very greatly in error. Therefore the graphical method suggested by Guggenheim[9] has been used to obtain the above values of k. While the accuracy obtainable in the rest of the work cannot be expected here, the results clearly indicate that any catalytic effect of the phenolate ion must be very small compared to the effect of the hydroxyl ion.

In all cases where catalytic effects by other acid molecules than hydrogen

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[8] Brönsted, *Chemical Reviews*, 5,286 (1928).

[9] Guggenheim, *Phil. Mag*, [7] 2, 538 (1926).

ions or by other basic molecules than hydroxyl ions, have been found, a water or spontaneous reaction has been found to occur.[10] Because of the slight catalytic effect of the phenolate ion, an attempt was made to determine the spontaneous reaction in the case of diacetone alcohol. The experiment was carried out in acid solution with a hydrogen-ion concentration of 1×10^{-5} mole per liter in a sealed dilatometer of the type used by Bronsted, Kilpatrick and Kilpatrick.[11] The reaction was very slow, but from the calculation from the total volume change in *a* suitable experiment with sodium hydroxide, it was estimated that the velocity constant 0.434 k was less than 3×10^{-7} min.$^{-1}$. This corresponds to a half time of more than 800 days. With the very slight catalytic effect of the phenolate ion, a negligible water reaction was to be expected.

A calculation of the classical dissociation constant of phenol at 0.2 M salt concentration is possible from the results in buffer solutions. The hydroxyl ion concentration is obtained by dividing the observed velocity constant by the constant for molal hydroxyl ion at the same electrolyte concentration. In the absence of a specific linear equation for the salt effect of sodium phenolate, the molal constant has been calculated from the equation

$$0.434\ k_2 = 0.215 - 0.074m$$

which was found previously to serve for chlorides. This was chosen because sodium chloride was used as the salt in the buffer solutions to keep the constant total electrolyte concentration of 0.2 M. From this, we get

$$[\mathrm{OH}^-] = \frac{2.02 \times 10^{-5}}{0.200} = 1.01 \times 10^{-4} \text{ moles per liter}$$

using 2.02×10^{-5} as the average of the observed values of 0.434 k in Table VI. The concentration of hydrogen ions in the solution is then calculable from the relation

$$[\mathrm{H}^+] = K_w/[\mathrm{OH}^-]$$

Brönsted[12] predicted that the rapid decrease in the activity coefficients of the ions of a weak electrolyte must lead to an increase in the dissociation constant. Harned and others[13] have confirmed this prediction by the measurement of suitable cells and have calculated the dissociation constant of water in the presence of various alkali salts. If we take from the measurements mentioned a probable value at 0.2 M salt concentration of 1.95×10^{-14} as the value for K_w on the basis of 1.005×10^{-14} for

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[10] Kilpatrick, This Journal, 50, *2891 (1928);* Bronsted, *Proc. Faraday Soc.*, November *(1928).*

[11] Bronsted, Kilpatrick and Kilpatrick, This Journal, 51, 428 *(1929).*

[12] Brönsted, *J. Chem. Soc., 119, 574 (1921).*

[13] Harned, This Journal, 47, *930 (1925);* Harned and Swindells, *ibid.*, 48, *126 (1926);* Åkerlöf, *ibid., 48,* 1160 *(1926);* Harned and James, *J.* Phys. *Chem.*, **30,** *1060 (1926)*; Harned, *Trans. Faraday Soc.*, *No.* 77, **23,** August *(1927).*

the value of K_w in water of zero salt concentration, we can now calculate the H-ion concentration in our buffer solutions.

$$[H^+] = \frac{1.95 \times 10^{-14}}{1.01 \times 10^{-4}} = 1.93 \times 10^{-10} \text{ moles } \textit{per liter}$$

Then the dissociation constant of the phenol in 0.2 M salt solution can be calculated.

$$K_{\text{phenol}} = \frac{[H^+][\text{phenolate}^-]}{[\text{phenol}]} = [H^+] = 1.93 \times 10^{-10}$$

The value for the dissociation constant of phenol at 25° given in the literature is 1.09×10^{-10}.[14] This value was determined by conductance and refers to zero salt concentration. Since phenol is a weak electrolyte, its dissociation constant would be expected to increase in salt solution, as has been found here. The great extent to which K_c varies with the salt concentration shows the necessity of stating the region of salt concentration in which the "constant" is to serve as the measure of acid or base strength. This same point has been shown in a study of secondary salt effects on the rate of decomposition of nitrosotriacetone-amine.[15] Consequently, values of K_c determined by methods such as have been used here for the given salt concentrations at which they were determined, should be much better than values of K_c which do not take this factor into consideration.

The decomposition of diacetone alcohol by other bases is being investigated and will be the subject of a later communication.

The author is indebted to Dr. and Mrs. Martin Kilpatrick, Jr., for the determination of the rate of the spontaneous decomposition of diacetone alcohol.

Summary

1. The velocity of decomposition of diacetone alcohol in solutions of sodium and potassium hydroxides has been measured at 25°. The hydroxide concentration was decreased from 0.1 to 0.01 M and it was found that over this range the velocity is proportional to the concentration of the hydroxide. The wide deviation from a rate proportional to the activity of the hydroxide has been shown.

2. The decomposition rate has been measured in 0.05 M hydroxide solutions in the presence of various alkali salts. The molal velocity constant varies linearly with the total equivalent salt concentration up to a total concentration of 0.25 M, as predicted by the Rronsted theory. The linear equations obtained depend only on the anion of the salt present, when the cations of the base and the salt are the same. There appears to be no regular relation between the magnitude of the salt effect and the concentration of the catalyst.

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[14] Lunden, *Z. physik. Chem.*, 70, 249 (1910).

[15] *Bronsted and* King, THIS *JOURNAL*, 47,2530 (1925).

3. A few measurements were carried out with phenol–sodium phenolate buffer solutions to investigate the possibility of catalysis by the phenolate ion. If present, such catalysis must be quite small compared to the hydroxyl ion catalysis.

4. If this reaction has a spontaneous water reaction, its half time is greater than 800 days.

5. A value of 1.93×10^{-10} for the dissociation constant of phenol in 0.2 molal salt solutions was calculated.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY]

OXIDATION OF SELENIUM DIOXIDE AND OF TELLURIUM DIOXIDE WITH LEAD DIOXIDE[1]

BY FRANK C. MATHERS AND FRANK V. GRAHAM[2]

RECEIVED APRIL 15, 1929 PUBLISHED NOVEMBER 8, 1929

Introduction

DeCarli[3] tested the action of lead dioxide in the dry state upon several other oxides at temperatures varying from 250 to 300°. Barium, cuprous, stannous, ferrous, manganous, cobaltous and nickelous oxides reacted with the lead dioxide to form higher oxides. The lead dioxide was reduced to the monoxide. There was no evidence of reaction with calcium, cadmium, plumbous, zinc, magnesium, cupric, aluminum and titanium oxides. The less metallic oxides like arsenious, antimonous, chromium, molybdenum and tungsten reacted with the lead peroxide to form lead salts of the type of lead arsenate, lead antimonate, etc. He concluded that lead dioxide had a notable tendency to react with other oxides at relatively low temperatures.

This research was merely an extension of the above reaction to include selenium dioxide and tellurium dioxide, two oxides that had not been tried by DeCarli.

Lead selenate can be changed[4] easily to ammonium selenate. The ammonium selenate thus formed can be changed[5] into other selenates by crystallizing solutions of it with various metallic nitrates. The lead tellurate can be changed by sulfuric acid into telluric acid. There have been, heretofore, only indirect methods[6] of making lead selenate and lead

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[1] From the thesis for the degree of Master of Arts by Frank V. Graham at Indiana University, 1928.

[2] Professor of Chemistry, Ball State Teachers College, Muncie, Indiana.

[3] DeCarli, *Gazz. chim. ital.*, **56,** 55 (1926); *C. A.*, 20, 1766 (1926).

[4] Mathers and Bonsib, THIS JOURNAL, **33,** 703 (1911).

[5] Unpublished work.

[6] (a) Becker, *Ann.*, **180,** 257 (1876); (b) Mathers, THIS JOURNAL, **30,** 1374 (1908); *(c)* Meyer and Moldenhauer, *Z. anorg. allgem. Chem.*, **116,** 193 (1921).

tellurate. Short direct methods for the rapid preparation of these salts are desirable as furnishing materials for making various selenates and tellurates.

Materials Used.—Two different samples of lead dioxide were used, one containing 90.09 and the other 94 94% of lead dioxide. The purity was always considered in calculating the weight to be used for a reaction.

Pure selenium dioxide was made by dissolving metallic selenium in nitric acid. This solution was filtered through asbestos and was then evaporated to dryness. The selenium dioxide thus formed was dissolved in water and filtered. This filtrate was evaporated to dryness and the solid selenium dioxide was sublimed. Its purity by analysis was 99.9%.

Tellurium dioxide was made by dissolving the 'commercial tellurium dioxide in hydrochloric acid. This strong acid solution was filtered through asbestos. The filtrate was hydrolyzed by the addition of a large volume of water. This precipitate of tellurous acid was washed and dried. Analysis showed its purity to be 98%

The ammonium carbonate was the ordinary "ammonium carbonate" commonly bought for laboratory use.

Methods of Analysis.—The selenates and tellurates were determined by the iodometric method of Gooch and Howland.[7] The selenite and the tellurite were determined by the potassium permanganate method of Brauner.[8]

Reaction of Selenium Dioxide with Lead Dioxide.—Preliminary experiments at 90, 100, 110 and 120° showed that very satisfactory results could be obtained at 100°. The rest of the experiments were made at this temperature because of the ease with which the 100° could be maintained on a steam-bath.

Two ways were tried for obtaining intimate contact between the reacting substances. The "dry" way was to grind the dry materials thoroughly together in a dry mortar. The "wet" way was to grind the ingredients thoroughly in the mortar with just enough water to give a thick paste. The various samples were then placed in small beakers and set in the steam-bath.

TABLE I

VARIATION IN QUANTITY OF LEAD DIOXIDE AND IN TIME OF HEATING

Formula weights of PbO_2 to one of SeO_2	Selenium dioxide changed to selenate, %					
	0 5 hour		3 hours		12 hours	
	Wet	Dry	Wet	Dry	Wet	Dry
1	91.8	88.5	94.6	92.5	98 9	93.1
1.05	97.9	93.5	98.3	94.5	97.9	95.3
1.1	97.7	94.6	99.5	95.8	99.9	96.1

The "wet" sample containing the 10% excess of lead dioxide was practically completely converted to selenate by heating for three hours or longer in the steam-bath. The "dry" mixed samples were not so com-

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[7] Gooch and Howland, *Z. anorg. allgem. Chem.*, **7**, *132* (1894); Am. J. *Sci.*, [3] *48*, 375 (1894).

[8] Brauner, J. *Chem. Soc.*, **59**, 240 (1891).

pletely oxidized. It is thought that the better oxidation of the "wet" mixtures was due entirely to better contact. At the end of the experiments the water had been completely evaporated from all of the beakers and the residues were all dry. The results shown in this table are entirely satisfactory. This is the best method yet described for making lead selenate.

Making Ammonium Selenate from the above Lead **Selenate.**—A previous paper[4] showed that ammonium selenate can be made easily by the digestion of lead selenate with ammonium carbonate. The lead selenate in those experiments was prepared by precipitation and was pure. This lead selenate was made by a dry method and was not pure. This difference in the physical condition of the lead selenate made desirable new experiments on its action with ammonium carbonate. Five grams of lead selenate and **3** g. of "ammonium carbonate" were used. This was a ratio of one formula weight of lead selenate to about 2.6 "CO_3" radicals.

TABLE II

CONVERSION OF LEAD SELENATE INTO AMMONIUM SELENATE

Water, cc.	Temp., °C.	Time in hours	Selenate obtained as ammonium selenate, %	
			Unstirred	Stirred
25	25	1	74.1	84.6
25	25	2	85.0	90.7
20	25	1	79.7	89.8
20	25	2	85.0	95.9
15	25	1	82.2	93.4
15	25	2	92.6	97.5
10	25	1	80.6	95.1
10	25	2	90.6	97.3
10	47	1	93.0	99.1
10	47	0.5	90.6	98.3
10	47	0.25	87.9	97.5
10	47	0.083	84.6	94.3

The yields were determined by filtering, washing the residues of lead carbonate and unchanged lead selenate with water and analyzing the filtrates for selenate. In the column marked "unstirred" the beakers were not agitated after the beginning of the experiment but the ammonium carbonate was dissolved before starting the experiment. In the column marked "stirred" a mechanical stirrer kept the mixtures in motion during the entire experiment. The table shows a yield of 99% using 10 cc. of water, 5 g. of lead selenate, *3* g. of ammonium carbonate, a temperature of 47° and stirring for one hour.

Crystals of ammonium selenate were easily obtained by evaporating the filtrate from this action of ammonium carbonate upon the lead selenate.

Reaction of Tellurium Dioxide with Lead Dioxide.—The amount of mixing of the tellurium dioxide and the lead dioxide affected the degree of oxidation. The materials in Table III were ground together in a dry mortar for one minute.

TABLE III

TELLURIUM DIOXIDE WITH LEAD DIOXIDE

Formula weights of PbO_2 to one of TeO_2	Temp., °C.	Tellurium dioxide converted into tellurate, % 1 hour	2 hours
1	300	62.9	71.2
1	205	58.6	79.2
1	170	85.1	89.8
1.05	170	93.5	93.7
1.1	170	98.1	99.8
1.1	155	89.7	92.7
1.1	185	94.1	97.5

This table clearly shows that 10% excess of lead dioxide is desirable and that 170° is the best temperature. Further experiments relative to the effect of the degree of mixing showed that the addition of enough water to form a paste after the tellurium dioxide and the 10% excess of lead dioxide had been ground together gave a yield of 99.5% at 170° for one hour. This result is compared to 97.3% when no water was used. However, grinding of the dry materials for two minutes gave the same yield of 99.9%.

Pure telluric acid was made from this lead tellurate by treatment with enough sulfuric acid to combine with all of the lead present in the mixture. This is a well-known old method.[6a] Three grams of sulfuric acid was used for each 10 g. of the lead tellurate mixture. All the telluric acid became soluble. The filtrate was evaporated nearly to dryness and the telluric acid was precipitated by an excess of nitric acid. The supernatant liquid was decanted and the residue was washed with a little concd. nitric acid to remove all the sulfuric acid. The residue was warmed on a water-bath until the nitric acid volatilized. This residue was dissolved in water and pure crystals of telluric acid, $H_2TeO_4 \cdot 2H_2O$, were prepared by slow evaporation.

Summary

1. The oxidation of selenium dioxide to selenate by heating with lead dioxide has been investigated under various conditions. The reaction proceeds very satisfactorily at 100°, the degree of completion varying with the time of heating and the mixing of the sample. The lead selenate produced may be converted to ammonium selenate by digestion with ammonium carbonate, followed by crystallization.

2. The process has been applied to the oxidation of tellurium dioxide, the optimum temperature being 170°. The yield varies with the amount of lead dioxide used and the intimacy of mixing of the sample taken. Telluric acid may be prepared from the lead tellurate produced by treatment with sulfuric acid and subsequent crystallization.

BLOOMINGTON, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

THE OXIDATION OF CALCIUM TELLURITE BY HEATING AND THE PREPARATION OF TELLURIC ACID PROM THE CALCIUM TELLURATE[1]

BY FRANK C. MATHERS AND GAIL M. BRADBURY[2]

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Synopsis.—Tellurium dioxide mixed with five equivalents of calcium hydroxide was almost completely oxidized to calcium tellurate by heating for one hour at 975°. The percentage oxidation was less at lower temperatures and with smaller proportions of calcium hydroxide. The calcium tellurate thus formed was treated with an excess of concentrated nitric acid, whereby soluble calcium nitrate and insoluble telluric acid were formed. This telluric acid, after filtration or decantation, was dissolved in water and crystallized until pure.

Review.—Many methods are described in the literature for oxidizing tellurium or tellurium dioxide to telluric acid. Perhaps the method most generally used was suggested by Staudenmaier.[3] The tellurium dioxide, in nitric acid solution, is oxidized with chromic acid. The separation of the telluric acid from the chromium nitrate is rather slow and difficult. The slowness and the complexity of this method, commonly considered the best, is a proof of the difficulty of making telluric acid. All of the methods proposed can be criticized from the standpoint of expensive or difficultly obtainable reagents, of difficulties in manipulation, of the introduction of troublesome impurities or of low yields.

Aim of this Research and Outline of the Method.—The method developed in this research was based upon the observation of Lenher and Wolesensky[4] that many tellurites are oxidized to tellurates by heating in the air. However, they found that sodium or potassium tellurite required heating for fifty hours at 460° for complete oxidation.

The purposes of this research were, first, to improve the method of Lenher and Wolesensky for the oxidation of tellurites by heating; second, to find a suitable way of preparing telluric acid from these tellurates.

The extreme slowness of the oxidation in their experiments was thought to be due the fusion of the salts, whereby only the surface of the mass was exposed to oxygen. Calcium tellurite, or a mixture of it with hydrated lime, was heated in these experiments. Such a salt or mixture remained porous during the heating and therefore allowed more rapid oxidation.

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[1] From the thesis for the degree of Master of Arts by Mr. Gail M. Bradbury at Indiana University, 1928.

[2] Teacher of Chemistry in Lakewood (Ohio) High School.

[3] Staudenmaier, Z. *anorg. Chem.*, 10, 189 (1896); Meloche and Woodstock, THIS JOURNAL, 51, 172 (1929).

[4] Lenher and Wolesensky, *ibid.*, 35, 729 (1913).

Method of Analysis.—The method of Brauner[5] using potassium permanganate was employed for the determination of the tellurite. The iodimetric method of Gooch and Howland[6] was used for the determination of the tellurate.

Materials Used.—The commercial tellurium dioxide[7] contained 49.59% of tellurium dioxide, 46.12% of sodium tellurite and 0.9% of selenium. This material was dissolved in concentrated hydrochloric acid and the solution thus formed was filtered through asbestos. The filtrate was evaporated to a small volume. The tellurium hydroxide or tellurous acid was precipitated by hydrolysis with a large volume of water. The precipitate was washed until free from chlorides and dried. This purified tellurium dioxide was a heavy, finely divided, slightly yellow powder.

The calcium hydroxide was a commercial high calcium "chemical" hydrated lime.

Experimental

All heating, unless otherwise noted was done in a Hoskins electric muffle furnace. The temperatures were measured with a platinum–rhodium thermocouple.

The tellurium dioxide and the lime were thoroughly mixed on a paper and then ground together in a mortar. The final mixtures, weighing from 10 to 30 g., were heated in small porcelain dishes. After heating, the entire mass of each mixture was ground to insure an accurate sample for analysis.

In all the early experiments, the heating was done at rather low temperatures because Lenher and Wolesensky had used 460°. It was soon found that the speed of oxidation increased as the temperature increased. A mixture of one formula weight of tellurium dioxide to two formula weights of calcium hydroxide was used in Table I.

TABLE I

EFFECT OF INCREASE OF TEMPERATURE

Temperature, ° C.	475	575	675	775
Heating, hours	25	25	20	5
Oxidation, %	21.4	44.7	64.7	39.3

The use of sodium carbonate with the calcium hydroxide and the tellurium dioxide greatly increased the speed of oxidation. However,

TABLE II

EFFECT OF SODIUM CARBONATE

Ratio of formula weights of	TeO_2	1	1	1	1	1
	$Ca(OH)_2$	1	1	1	0	0.5
	Na_2CO_3	0	0.1	0.5	1	1
Time of heating, hours		15	15	15	5	5
Oxidation percentage		12.6	46.4	84.7	36.9	99.1

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[5] Brauner, J. Chem. *Soc.* 59, 238 (1891).

[6] Gooch and Howland, *Z.* anorg. *chem.*, 7, 132 (1894); *Am. J. Sci.*, [3] 48, 375 (1894).

[7] The authors wish to thank Mr. Skowronski of the Raritan Copper Company, Perth Amboy, New Jersey, for furnishing this material.

sodium carbonate without the lime was not satisfactory as is shown by Expt. 4 in Table II. The temperature of the experiments recorded in this table was 575°.

Although the rapidity and the completeness of oxidation of these mixtures containing sodium carbonate and hydrated lime were entirely satisfactory, the presence of the sodium salts made difficult the preparation of the pure telluric acid.

Table III

Effect of Higher Temperatures and Greater Proportions of Calcium Hydroxide

Formula weights of calcium hydroxide to one of TeO_2	3	4	5	0	8	5	6
Temperature, °C.	975	975	975	975	975	1075	1075
Heating, hours	5	5	5	5	5	5	5
Oxidation, %	817	894	97.5	95.8	94.9	99.8	974

This table shows that the ratio of five formula weights of calcium hydroxide to one formula weight of tellurium dioxide is sufficient for maximum oxidation; also, that a temperature of 975° is sufficient, although 1075° does not lessen the yield through decomposition. The stability of the calcium tellurate at this high temperature was a great surprise.

Experiments were then made to determine the optimum time of heating required under these other optimum conditions of 975" and a mixture containing five formula weights of calcium hydroxide to one formula weight of tellurium dioxide.

Table IV

Time of Heating Required

Heating, hours	025	0 5	1	2	4	5	6
Oxidation, %	93.6	957	98.7	98.8	99.3	98.7	98.1

Based upon experiments in which silver strips (melting point 960°) were embedded at different places in the mixtures being heated, it is thought that oxidation is practically complete as soon as the temperature has reached-975" throughout the mass.

Heating in a gas-fired pot furnace at a final temperature of 1100° gave about as good results as the careful heating in the electric furnace. A 25-g. mixture gave 98.1% oxidation in one hour. A 230-g. mixture gave 87.2% oxidation in two hours. These lower yields with the larger samples indicate that there was not enough air circulating through the mass. One important point that favors this method is that a carefully controlled heating temperature is unnecessary; it is important only to heat at 975 to 1100". Higher temperatures could not be tried with the methods of heating that were available.

Barium hydroxide and barium carbonate mixtures with the tellurium dioxide gave almost no oxidation. Calcium carbonate gave as good results as calcium hydroxide under the same conditions.

Preparation of Telluric Acid from the Calcium Tellurate.—A description of one quantitative experiment will suffice to make clear the general conditions and method of operation for easily making telluric acid crystals. Seventy-five grams of the tellurium dioxide and 177 g of calcium hydroxide (a 1:5 mixture) were placed in a clay crucible and heated in a gas furnace for a total of two hours with the final temperature reaching 1100°. The percentage oxidation was 88.5. Two hundred grams of this mixture was treated with 300 cc. of concentrated nitric acid, heated to boiling and cooled overnight. The supernatant liquid was decanted and 200 cc. more concentrated nitric acid was added to the residue of telluric acid. This was heated to boiling, cooled and again the supernatant liquid was decanted. The residue of telluric acid was dissolved in hot water and filtered to remove traces of insoluble matter. This filtrate, after evaporation to a small volume, smelled strongly of nitric acid. Again, after cooling overnight, the liquid was decanted. The residue of telluric acid was dissolved in water and crystallized. The weight of the pure crystals of telluric acid equaled 75.4% of the total telluric acid in the material used. The exact quantities of the acid used in this experiment need not be followed. Indeed, less nitric acid can be used in the washing. No research was made to determine the best quantities of reagents for the maximum yields.

Attempts to decompose the calcium tellurate with dilute sulfuric acid, whereby calcium sulfate was precipitated, were unsuccessful. So much calcium sulfate always remained in solution that its final separation from the telluric acid was difficult. Carbon dioxide or oxalic acid would not decompose the calcium tellurate.

It is possible to treat the calcium tellurate with an equivalent amount of nitric acid, evaporate to dryness and extract the calcium nitrate from the residue with alcohol, in which the telluric acid is insoluble.

The authors wish to thank the Grasselli Chemical Company for their fellowship, which was held by Mr. Bradbury during the progress of this work.

Summary

Maximum speed and completeness of oxidation were obtained by heating a mixture of one formula weight of tellurium dioxide with five formula weights of hydrated lime at 975 to 1075° for an hour.

Telluric acid was easily prepared from the calcium tellurate thus formed by the addition of an excess of concentrated nitric acid. The soluble calcium nitrate was decanted from the precipitate of crude telluric acid. Pure telluric acid was obtained from this residue by crystallization from water.

BLOOMINGTON, INDIANA

[Contribution from the School of Chemistry, University of Minnesota]

GRAVIMETRIC DETERMINATION OF SODIUM BY THE URANYL ZINC ACETATE METHOD. II. APPLICATION IN THE PRESENCE OF RUBIDIUM, CESIUM, POTASSIUM, LITHIUM, PHOSPHATE OR ARSENATE

By H. H. Barber and I. M. Kolthoff

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In the first paper[1] of the general procedure for the determination of sodium by the uranyl zinc acetate method, it was shown that the method is quite specific for sodium, though lithium and large amounts of potassium have an interfering action. As the determination of sodium in the presence of other alkali metals is of great practical importance, we present in this paper the results of a study made in this direction. With regard to the interfering anions, we consider especially the removal of the phosphate and arsenate ions.

Rubidium and Cesium.—A solution of 100 mg. of pure rubidium chloride and cesium chloride, respectively, in 1 cc. of water does not give a precipitate with 10 cc. of the reagent after long standing. It was shown that Kahlbaum's salts of these elements contained a trace of sodium: the rubidium chloride, 0.45%; the cesium chloride, 0.13%. The general procedure outlined in the first paper is to be followed in determining sodium in rubidium and cesium compounds.

Potassium.—In the first paper it was shown that if a solution contains more than 50 mg. of potassium per cc., potassium uranyl zinc acetate will be precipitated; therefore, in cases where sodium is to be determined in large amounts of potassium, the larger part of the latter has to be removed.[2] It is not necessary to remove all of the potassium in a quantitative way, as small amounts of this element do not interfere with the sodium determination. For the precipitation of the larger part of potassium, we used ammonium perchlorate in a medium of 72% alcohol. A test for purity of the ammonium perchlorate is made by dissolving 1 g. of the salt in 10 cc. of the reagent. A clear solution should be ob-

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[1] Barber and Kolthoff, This Journal, 50, 1625 (1928).

[2] In order to avoid any misunderstanding, it may be remarked that if more than 50 mg. of potassium per cc. is present, the solution can be correspondingly diluted, provided that in the precipitation of sodium for each cc. of solution 10 cc. of the reagent is used. If the ratio of sodium to potassium is very unfavorable, the application of the above procedure would require large amounts of reagent and therefore would be uneconomical and impracticable.

In the general procedure for the precipitation of sodium, it should be noted that as long as a ratio of 1 cc. of solution to 10 cc. of reagent is maintained, satisfactory results will be obtained. Each 10 cc. of reagent will completely precipitate from 1 cc. of solution 8 mg. of sodium. If 5 cc. of solution were used, 50 cc. of reagent should be added. This amount of reagent would precipitate, if present, 40 mg. of sodium.

tained with no separation of crystals after standing for one hour. If the perchlorate contains sodium, the latter can be removed easily by recrystallization from water.

Procedure

One gram of potassium chloride is dissolved in 5 cc. of water. To this add a hot solution of 2 g. of ammonium perchlorate in 3 cc. of water and 25 cc. of 95% alcohol. Cool the mixture to room temperature, filter and wash the precipitate five times carefully with 2-cc. portions of 95% alcohol. Evaporate the filtrate to dryness, take the residue up in 1 cc. of water and add 10 cc. of reagent. If the potassium salt contains more than 1% of sodium, the residue should be taken up in more water and an aliquot part weighed out. As a matter of fact, one may start in this case with less potassium salt. A qualitative test for sodium in the potassium salt will give an approximate idea of the amount of sodium present (see first paper). The following table shows that traces of sodium down to 0.1% may be determined in potassium chloride with an accuracy of 1 to 2%.

TABLE I

DETERMINATION OF TRACES OF SODIUM IN THE PRESENCE OF 1 G. OF POTASSIUM CHLORIDE

NaCl, g.	Wt of ppt , g	NaCl calcd from ppt , g	NaCl, g	Wt of ppt , g	NaCl calcd from ppt , g.
0.01414	0.3667	0.01394	0.0064	0.1692	0.0064
.01289	.3367	.01280	.0057	.1540	.0058
.01197	.3104	.01180	.0055	.1477	.0056
.01063	.2812	.01068	.0046	.1160	.0044
.0085	.2278	.0086	.0044	.1164	.0044
.0079	.2103	.0080	.0043	.1073	.0041
.0079	.2036	.0077	.0039	.1003	.0038
.0077	.2028	.0077	.0037	.0954	.0036
.0077	.2034	.0077	.0023	.0597	.0023
.0070	.1794	.0068	.0020	.0520	.0020

It should be mentioned that the outlined procedure is useful for the qualitative detection of traces of sodium in potassium salts. In that case it is not necessary, of course, to wash the potassium perchlorate with alcohol.

In the way described 0.005% of sodium can easily be detected in potassium salts.

Lithium.—Many more difficulties were encountered in the determination of sodium in the presence of lithium. Lithium triple salt is very slightly soluble. A solution of 0.2 mg. of lithium in 1 cc. of water with 10 cc. of reagent forms a crystalline deposit after a few hours' standing. The reaction would be more sensitive if the reagent was saturated to the lithium compound. We are planning to make a study on the application of the reagent for the determination of lithium.

For the determination of sodium in the presence of lithium, the latter has to be quantitatively removed. We first tried the alcohol–ether method of S. Palkin,[3] but did not find this method suited to our purpose as in his

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[3] Palkin, THIS JOURNAL, 38, 2326 (1916).

procedure all the alkali metals have to be in the form of chlorides. Commercial salts of lithium and even C. P. products appeared to contain sulfate as an impurity; it is necessary to remove this anion, as lithium sulfate is insoluble in the alcohol–ether mixture. The extraction method in the regular course of analysis will give satisfactory results. In cases where traces of sodium have to be determined in lithium compounds, we prefer to remove the latter in the form of an insoluble salt; therefore, we precipitated lithium as the fluoride.

In our first experiments we attempted to purify C. P. products of lithium chloride according to the alcohol–ether method of Palkin.[3] The purified salt still contained traces of sodium.[4] A better product for our purpose was obtained by precipitation of lithium as a carbonate with pure ammonium carbonate.

The separation of sodium from lithium by-the fluoride method is a tedious procedure. Though the solubility of lithium fluoride in water is small, alcohol should be added to precipitate the lithium quantitatively. However, if too much alcohol is added, or if too much lithium is present, some sodium may be carried down by the precipitate. On the other hand, if too little alcohol is added, too high results are found due to incomplete precipitation of lithium. Under special conditions a compensation of errors may lead to results agreeing with the theoretical.

TABLE II

SEPARATION OF LITHIUM PROM SODIUM

Concn. of alcohol, %	NaCl, g.	LiCl, g.	NaCl found, g.	Error, %
10	0.05712	0.10	0.05887	+3.0
15	,05903	.05	.06224	+5.4
15	.05850	.22	.05840	−0.2
15	.06004	.33	.05828	−3.0
20	.06048	.22	.05743	−5.0
25	.05860	.22	.05495	−6.6
25	.06145	.24	,05607	−9.0
30	.05741	.22	.05029	−12.5
40	.06935	.10	.06709	−3.3

In the final procedure a 10% solution of ammoniacal ammonium fluoride was used. (The reagent should be kept in paraffined or hard rubber bottles.) The ammonia has to be added to decompose fluosilicate, which occurs as an impurity even in chemically pure products of ammonium fluoride and interferes in the separation, and also to prevent the action of the fluoride on glass. A 25% solution of hydrochloric acid and 95% alcohol are the other reagents.

Though ammonium fluoride does not precipitate with uranyl zinc acetate, it prevents the precipitation of sodium; therefore, the fluoride

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[4] Compare, also, T. W. Richards and H. H. Willard, THIS JOURNAL, 32, 4 (1910).

has to be removed before the sodium is precipitated with the reagent. This can be done easily by evaporation with hydrochloric acid. The ammonium fluoride and hydrochloric acid should be tested for purity. In a platinum crucible place about 1 g. of ammonium fluoride, add 10 cc. of 25% hydrochloric acid and evaporate to dryness. Add to the residue 5 *cc.* of the reagent and transfer to a test-tube. The solution should be clear after standing for one-half hour. The ammonium hydroxide used has to be sodium free. Evaporate 5 cc. to dryness and test residue with the reagent. All the solutions of ammonia tested contained sodium. It was necessary to redistil and keep in paraffined bottles.

Procedure

To not more than 0.1 g. of the salt add 10 cc. of water and 5 cc. of 95% alcohol. After the salt has dissolved, add 5 cc of the ammonium fluoride solution. Allow to stand for twenty hours, or longer, and then filter off the precipitate through a glass filter crucible. The lithium fluoride is washed five times with 2-cc. portions of a 50% alcohol solution containing 0.5% of ammoniacal ammonium fluoride. The filtrate and wash liquor are evaporated carefully in a platinum crucible and the residue is evaporated three times with 5-cc. portions of hydrochloric acid. The residue is now transferred with water to a weighing bottle of known weight. The solution is evaporated to a volume of 2 to 5 cc. and weighed after cooling. An aliquot part is weighed out and the sodium determined by the regular procedure.

If amounts of sodium of the order of 1.5% or less have to be determined in lithium salts, one may start with 0.5 g. of salt and treat this according to the above procedure. Finally, the residue is taken up in 2 cc. of water and 20 cc. of uranyl zinc acetate reagent is added. In this way we found that sodium could be determined with an accuracy of 1 to 2%.

TABLE III

SEPARATION OF LITHIUM PROM SODIUM

Concn. of alcohol, %	NaCl, g.	LiCl, g.	NaCl found, g.	Error, %
25	0.06306	0.02	0.06321	+0.2
25	,05894	.08	,05888	− .1
25	.05941	.10	,05917	− .4
25	.1135	.10	.1138	+ .3
25	.005936	.35	.00607	+2.0
25	.003994	.38	.00392	−2.0

In Tables II and III the analyses show that when the alcohol concentration is 25%, good results are obtained if the ratio between weight of sodium chloride taken and weight of lithium chloride is 1 to 1 or less where the weight of sodium chloride is 100 mg., or less. However, as soon as the ratio between the weight of sodium chloride and weight of lithium chloride becomes 1 to 2, sodium is carried out of the solution by the lithium fluoride precipitate and low results are obtained. On the other hand, results within 2% of the theoretical were obtained when a few mg. (4–6 mg.) of sodium chloride was present with a much greater quantity (350 mg.) of lithium fluoride.

All of our experimental work in 25% alcohol solution gave consistently low values for sodium when the sodium chloride–lithium chloride content in 20 cc. of solution was 100 mg., or less, of sodium chloride to 125 mg., or more, of lithium chloride (see Table II), but when the lithium chloride content was 100 mg., or less, excellent results were obtained (see Table III). Consequently, the amount of lithium chloride should not be greater than 100 mg. in 20 cc. of 25% alcohol solution unless small amounts, a few mg., of sodium are to be determined in lithium salts. In this case, 0.3 to 0.4 g. of lithium chloride may be present.

Phosphate and Arsenate.—Phosphate and arsenate give a precipitate with the uranyl zinc acetate reagent. We first tried to remove these ions with a dilute solution of the reagent. (Sodium does not precipitate under these conditions.) However, this procedure cannot be recommended as the slimy precipitate absorbs sodium and too low results are obtained. It is better to remove the phosphate and arsenate by precipitation with magnesia mixture in cold solution to which an excess of ammonia has been added. The filtrate and the wash liquor are evaporated to dryness and the sodium is determined according to the regular procedure. Again, the reagents must be free from sodium and the usual precautions for precipitating phosphate or arsenate with magnesia mixture must be observed.

In our experiments we used monopotassium phosphate and dipotassium arsenate. Both salts were recrystallized three times from water. In the following table we show that satisfactory results are obtained.

TABLE IV

SEPARATION OF PHOSPHATE AND ARSENATE FROM SODIUM

K_2HPO_4, g.	NaCl, g.	NaCl, found, g.	Error, %	K_2HAsO_4, g.	NaCl, g.	NaCl found, g.	Error %
0.076	0.01143	0.01180	+3.0	0.033	0.01182	0.01182	0.0
.087	.01220	.01220	0.0	.086	.01259	.01260	+ .1
.034	.01199	.01210	+1.0	.048	.01124	.01130	+ .5
.019	.01048	.01053	+0.5				

Summary

The determination of sodium in the presence of the alkali metals, phosphate or arsenate has been investigated and the following ascertained.

1. Cesium and rubidium in amounts of 0.1 g. do not interfere.
2. Interfering amounts of potassium may be removed by precipitation with ammonium perchlorate in 72% alcoholic solution.
3. Lithium must be removed quantitatively. Ammonium fluoride in 25% alcoholic solution is used to precipitate the lithium.
4. Phosphate and arsenate interfere and are removed by precipitation with magnesia mixture.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

ZIRCONIUM. V. DETECTION OF TRACES OF POTASSIUM IN THE PRESENCE OF ZIRCONIUM[1]

BY RUFUS D. REED AND JAMES R. WITHROW

RECEIVED MAY 23, 1929 PUBLISHED NOVEMBER 8, 1929

Zirconium sulfate can be used to detect potassium,[2] but the completeness of precipitation of potassium by zirconium sulfate is not easily measured, as zirconium sulfate also gives a precipitate with sodium cobaltic nitrite. Obviously zirconium must be eliminated, if present, prior to testing for potassium, so a study of delicate methods of detection of traces of potassium under these conditions was made. The results indicated that while phosphates will remove the zirconium, they interfere with the subsequent detection of traces of potassium. Ammonium hydroxide, however, was found to remove all of the zirconium without interfering materially with subsequent detection of potassium. Also a quicker and less objectionable method was found to be the transformation of the zirconium into a complex ion with tartaric acid, and after adjusting the acidity with sodium hydroxide and acetic acid, testing for potassium with sodium cobaltic nitrite.

Discussion of Literature

Zirconium can be removed by phosphates in excess under proper condition~. Bray[4] found that dilute sodium phosphate solution gave no precipitate with sodium cobaltic nitrite; but according to solubility records[5] approximately 39 cc. of water at 20° would be needed to dissolve the 7.5 g. of sodium phosphate which we found was needed to remove 0.1134 g. of zirconium sulfate used in the test. If the original concentration of potassium was 1 mg. per cc., this dilution would lower the concentration to 0.02 mg. per cc.—a smaller concentration than sodium cobaltic nitrite will detect.[2]

Smaller concentrations of phosphoric acid, microcosmic salt or ammonium phosphate would remove the zirconium but the interfering ammonium salts would have to be expelled before testing for potassium. The gelatinous zirconium phosphate might adsorb any traces of potassium salts. The use of ammonium hydroxide to remove the zirconium risked the same objections.

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[1] Presented at the Columbus Meeting of the American Chemical Society, April 25, 1929.

[2] Reed and Withrow, THIS JOURNAL, 50, 1515 (1928).

[3] Reed and Withrow, *ibid.*, 51, 1311 (1929).

[4] Bray, *ibid.*, 31, 634 (1909).

[5] Seidell, "Solubility of Inorganic and Organic Compounds," D. Van Nostrand Co., New York, 2d ed., **1919**, p. 662.

The possibility of avoiding these dangers of loss of potassium by volatilization or adsorption, by the elimination of zirconium as a complex ion was suggested by the statement of Fresenius,[6] "tartaric acid prevents the precipitation (of zirconium) by alkalies."

Experimental

Detection of Potassium after Removal of Zirconium.—Samples containing 0.113 g. of zirconium sulfate, varying amounts of potassium and 1634 g. of hydrogen sulfate were prepared. Some were treated with an excess of 5 times the calculated needed amount of either phosphoric acid, ammonium phosphate or microcosmic salt. To avoid evaporation of large amounts of solution the final volume was kept at 50 cc. After standing for several hours the solutions were filtered and the filter washed four times with cold water. The filtrate and washings were evaporated to a sirup. This was transferred with washing to a platinum crucible, the evaporation continued to dryness and the residue ignited short of red heat until no more fumes were noticed. If a drop of a solution prepared by adding 1 cc. of water to the residue gave no test for ammonium salts with Nessler's reagent, the remainder was neutralized with sodium hydroxide, about 3 cc. of 30% acetic acid was added and then an equal volume of sodium cobaltic nitrite solution. Preliminary experimentation showed that if this excess acid was not added a flaky precipitate was obtained whether potassium was present or not. This amount of acetic acid did not prevent the detection of 0.3 mg. of potassium in a test solution. Other samples were treated with ammonium hydroxide instead of phosphates to remove the zirconium and the filtrates were tested for potassium in the same way except that no acetic acid was added. The results appear in Table I.

TABLE I

DETECTION OF POTASSIUM BY SODIUM COBALTIC NITRITE AFTER REMOVAL OF ZIRCONIUM

Expt.	K, g per sample	Results of test for potassium by $Na_3Co(NO_2)_6$ after removing zirconium by H_3PO_4	$NaNH_4HPO_4$	$(NH_4)_2HPO_4$	NH_4OH
1	0.00053	Flaky ppt.	Flaky ppt.	Clear. sev. hrs.	Ppt., 4 min.
2	.00031	Clear, 20 min.; cloudy, 2 hrs.	Ppt., 45 min.	Clear, no ppt., sev. hrs.	Ppt., 5 min.
3	.00012	Clear, no ppt., 1 hr.	Clear, no ppt., 1 hr.	Clear, no ppt., sev. hrs.	Sl. ppt., standing hrs.
4	.00000	Clear, no ppt., 15 min.; cloudy, 1 hr.	Clear, 1 hr.	Clear, 20 min.; cloudy, 40 hrs.	Clear, no ppt., 1 day
5	.00176	......	......	Ppt. at once	

Discussion.—The precipitates (Run 1) where zirconium had been removed by phosphoric acid or microcosmic salt were flaky and brownish, not the usual yellow color of potassium cobaltic nitrite. They resembled the precipitates obtained (preliminary work) by adding sodium cobaltic nitrite to a solution of phosphoric acid neutralized by sodium hydroxide which had added thereto but a small excess of acetic acid.

The results in Cols. 2, 3 and 4, where zirconium was removed by phosphates prior to testing for potassium, indicated that either the zirconium phosphate adsorbed the potassium or the prolonged heating, needed to

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[6] Fresenius, "Qualitative Chemical Analysis," translated by C. A. Mitchell, John Wiley and Sons, Inc., New York, 1921, 17th German ed., p. 181.

drive off the excess acids and ammonium salts, volatilized most or all of the potassium. When zirconium was removed by ammonium hydroxide (Col. 5), prior to testing for potassium, there were no such difficulties in detecting potassium. Therefore phosphates are not suitable and *ammonium hydroxide is suitable for removing zirconium prior to testing for potassium by sodium cobaltic nitrite.*

Detection of Potassium in the Presence of Zirconium by Changing the Zirconium into a Non-Interfering Complex Ion with Tartaric Acid.—Preliminary experimentation showed that if a 2-cc. solution of zirconium sulfate be treated with 0.3 g. of tartaric acid and the acidity controlled by neutralizing with 25% sodium hydroxide, making slightly acid with acetic acid, no precipitate is obtained with sodium cobaltic nitrite. If any potassium was added, a test for it was obtained. To determine the sensitiveness of sodium cobaltic nitrite for potassium under these conditions, a series of experiments was run. The manipulation was exactly as described above. The amount of zirconium sulfate was 0.1131 g. per test, the tartaric acid 0.3 g. and the amount of potassium varied. The results appear in Table II.

TABLE II

SENSITIVENESS OF SODIUM COBALTIC NITRITE FOR POTASSIUM WHEN ZIRCONIUM IS PRESENT IN COMPLEX ION

Expt.	K, g. per sample	Results of test for potassium with $Na_3Co(NO_2)_6$ Presence of zirconium	Absence of zirconium K_2SO_4 alone present
1	0.00107	Cloudy at once; ppt., 5 min.	Ppt., 5 min.
2	.00072	Cloudy, 5 min.	Sl. ppt., 5 min.
3	,00053	Cloudy, 10 min.	Very sl. ppt., 10 min.
4	.00030	Very sl. cloudy, 15 min ; ppt , 1.5 hrs.	Very sl. ppt., 10 min.
5	.00014	Very sl. cloudy, 1.5 hrs.; no ppt., 2 hrs.	Ppt., 2.5 hrs.
6	.00000	No ppt.; clear, 1.5 hrs.	Clear, no ppt., 23 hrs.

Discussion.—The suppression of zirconium by tartaric acid did not prevent the detection of 0.3 mg. of potassium (Expt. 4) by sodium cobaltic nitrite. The slight difference between the time for appearance of a precipitate in the test for potassium in the presence (Expt. 4) and absence of zirconium was doubtless due to dilution of potassium solution from 1 cc. to 3 cc. with zirconium present.

This method of suppression of zirconium ions is much to be preferred to removal of zirconium by either phosphates or ammonium hydroxide prior to testing for potassium by sodium cobaltic nitrite, as it is shorter and avoids danger of adsorption or volatilization of potassium.

Summary

1. The use of phosphates to remove zirconium prior to testing for potassium by sodium cobaltic nitrite is not advisable because of loss or dilution of potassium.

2. When phosphoric acid is neutralized with sodium hydroxide and the solution tested with sodium cobaltic nitrite, a misleading precipitate is secured unless a considerable excess of acetic acid is added.

3. Zirconium can be removed by ammonium hydroxide and potassium detected in the filtrate by sodium cobaltic nitrite, after eliminating the ammonium.

4. The best and shortest way of eliminating zirconium prior to testing for potassium by sodium cobaltic nitrite is by throwing the zirconium into a complex ion with tartaric acid and controlling the acidity with sodium hydroxide and acetic acid.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORY, UNITED VERDE COPPER COMPANY]

THE SYSTEM SODIUM SULFIDE–FERROUS SULFIDE[1]

BY L. V. STECK, MORRIS SLAVIN AND O. C. RALSTON

RECEIVED MAY 27, 1929 PUBLISHED NOVEMBER 8, 1929

This investigation deals with the composition diagram of the system Na_2S–FeS obtained from cooling curves on melts of several compositions and by microscopic examination of polished surfaces of frozen samples of the melts. The principal interest from an industrial standpoint was in the liquidus curves and no great effort was made completely to determine the nature of the phases or phase changes at temperatures beneath the liquidus. Therefore the phase diagram as presented is incomplete but contains the reasonable conclusions and certain inferences that seem to be justified by the data.

Preparation of Sodium Sulfide.—Several methods for preparing pure sodium sulfide were considered: reduction of sodium sulfate with carbon; the Hugot[2] method of reacting with sulfur on a solution of sodium in liquid ammonia with subsequent evaporation of excess ammonia; the Hugot method of reacting on molten sodium with hydrogen sulfide; the Sabatier[3] method of dehydrating the hydrated salt, $Na_2S\cdot 9H_2O$; and the reaction[4] obtained by heating sodium carbonate in sulfur vapor. All of these methods were tested by Friedrich,[5] who found that a reasonably pure product could be obtained by heating the hydrated salt in a rapid stream of hydrogen. The hydrated salt first melts in its water of crystallization, solidifying when the mass has reached about 70% of sodium sulfide by weight and leaving a porous mass from which the remainder of the

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[1] The preparation of materials and cooling curves was carried on in the Pacific Experiment Station of the U. S. Bureau of Mines, at Berkeley, California.

[2] Hugot, *Compt. rend.*, **129**, *388* (1899).

[3] Sabatier, *Ann. chim. phys.*, [5] **22**, *66* (1881).

[4] Vauquelin, *ibid.*, *[2]6*, **32** (1817).

[5] Friedrich, *Metall und Erz*, **11**, 79 (1914).

water evaporates. The solid material loses part of its sulfur by hydrolysis so that the final product contains sodium hydroxide. Friedrich's preparation melted at 920°. .

This latter method was used in the present investigation because it was the only convenient one by which large quantities could be prepared. The first stage of evaporation was done in a large vacuum desiccator with a small electric heater, whose temperature never exceeded 50°, leaving a product with about 80% of Na_2S. When heated to 150° the final product in the desiccator, when using phosphorus pentoxide as desiccant, contained about 95% of sodium sulfide. This material when melted in a graphite crucible under nitrogen (losing more water during the heating) and cooled slowly indicated by its cooling curve that it froze at 970°. The melting point of the pure material is probably slightly above this temperature.

Preparation of Pure Iron Sulfide.—Two methods were tested: the thermal decomposition of pure pyrite, FeS_2, and the synthesis from iron and sulfur by absorbing sulfur vapor in fused pure iron.

The first method was used by Mostovitsch[6] in preparing iron sulfide analyzing 63.67% of iron and 36.33% of sulfur; the theoretical analysis is 63.52% of iron and 36.48% of sulfur.

In this research some 200 g. of iron sulfide, analyzing 63.5% of iron and 36.4% of sulfur, was made by the following method. A large specimen of very pure Chinese pyrite was ground through 65 mesh, packed in a graphite crucible under charcoal and covered with a graphite cover. It was heated in an electric resistance furnace to 1000°, cooled, reground, repacked in the crucible, heated just above the melting point and cooled in the furnace. A small amount of siliceous slag that had floated to the top was broken off and discarded. The balance had a rainbow luster and could be broken with the fingers into eighth-inch pieces.

When larger quantities of the iron sulfide were required the limitations of the supply of pure pyrite necessitated the use of some other method of preparation. Approximately a hundred grams of Armco iron turnings was mixed with distilled sulfur and placed in a graphite crucible in an Ajax Northrup Induction Furnace. As the furnace heated, the iron and sulfur united and formed a molten pool into which Armco iron strips and sulfur were alternately fed until there was approximately 1500 g. of material in the crucible. Sulfur was then dropped on the molten material until no more was taken up by the melt, which could be determined by observation. The melt was cooled, ground through 65 mesh, mixed with sulfur and remelted. It was kept in the molten condition for ten minutes, the furnace action providing very efficient stirring. The current was shut off and the temperature was taken every thirty seconds, using the thermocouple arrangement described later. While a very sharp freezing point was not obtained (see Fig. 1), the iron sulfide solidified within a few degrees of 1174". Check analyses gave the composition as 62.84% of iron and 36.92% of sulfur; 99.95% total. Analysis for carbon and oxygen may show the remainder.

Carbon in varying amounts was known to be present in all the melts, coming from the Acheson graphite crucible in which the work was done. The theoretical analysis of pure iron sulfide calls for 63.52% of iron and 36.48% of sulfur. Our preparation therefore consisted apparently of 98.9% of iron sulfide with the remainder excess sulfur and a small amount of carbon. The excess sulfur is probably present as pyrrhotite,

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[6] Mostovitsch, *Ann. First Tomsk Siberian Technological Inst.*, [47] *1*, 1–74 (1925).

Fe_xS_{x+1}, where the subscript x is likely to have a high value. In the amounts of material with which we worked we did not arrive at a product which was slightly deficient in sulfur and which is reported by Allen and co-workers.? According to their experience ferrous sulfide dissociates slightly in the vicinity of its melting- point, losing sulfur by volatilization and leaving a material with a slight excess of free iron. They located the melting point of pure ferrous sulfide at 1170 ± 5°. Our slightly impure product gave an arrest in its cooling curve at 1174°, showing thereby very good agreement in thermometry with their work.

Apparatus.—Our mixtures of iron sulfide and sodium sulfide were melted in Acheson graphite crucibles with graphite lids in a high frequency induction furnace, the heat being generated by induced currents in the graphite crucibles. Crucibles of about 3 inches outside diameter and containing from 500 to 1000 g. of melt were used. They were placed in the center space of the induction furnace, which consisted of a vertical cylindrical tube of vitreosil around which was packed finely powdered electrically fused magnesia as an insulator. The bottom of the furnace was also of powdered magnesia. The thickness of this thermal insulation was about 3 inches and outside of everything were the copper tubing coils which constituted the inductors of the high frequency furnace. Sufficient electrical capacity was available to start cold and bring a melt to the desired temperature within five minutes, although the usual practice was to use three or four times as long an interval in order to establish a thermal diffusion gradient.

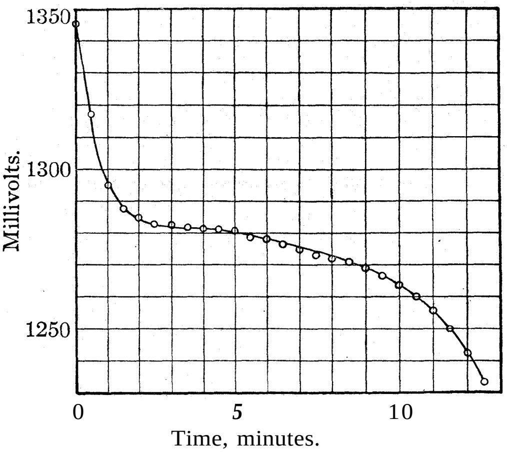

Fig. 1.—Cooling curve of FeS.

Temperatures were read with a platinum–platinum-rhodium couple, frequently calibrated against a similar standard couple which had been standardized by the Bureau of Standards. The Leeds and Northrup Type K potentiometer was used for e.m.f. measurements except where specified. The couple was protected by thin-walled chemical porcelain tubes manufactured especially for this work by Coors, the tubes having an outside diameter of 0.25 inch and being introduced into the melt through a small hole in the graphite cover of the crucible. Melts were not allowed to cool to the 298" polymorphic transition of iron sulfide because at this point the volume change was sufficient to crush the porcelain protecting tube. Therefore, after a cooling curve had been followed to about 400° the crucible was reheated until the protection tube could be withdrawn through remelting of the charge. A new porcelain tube was used with each melt, thereby maintaining adequate protection of the couple. The sodium sulfide was kept under nitrogen and the furnace was swept with nitrogen during melting and cooling. Sodium sulfide was weighed under nitrogen only after cooling with an ice-bath.

Results

In all, eleven cooling curves were obtained which could be used for preparing the phase diagram. The curve for pure iron sulfide, as shown in Pig. 1, has already been mentioned. The arrests in the other cooling

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[7] Allen and co-workers, **Am. J.** *Sci.,* [4] **33,** 169 (1912).

curves have been tabulated in Table I. Four of them were made with mixtures of iron sulfide and sodium sulfide and the remainder, which were higher in sodium sulfide content, were made by adding more sodium sulfide to the product of a previous melt which was merely reheated in the same crucible, to which was added the new sodium sulfide and a sufficient sample withdrawn for analysis.

TABLE I

EXPERIMENTAL DATA

Run	FeS, %	Arrests,		Materials	Remarks
		Primary	Eutectic		
7	98.6	1174		FeS	.. . . . .
10	93.5	1088	703–688	FeS + Na_2S	Used portable potentiometer. Eutectic crystals in center
11	86.4	....	694–674	FeS + Na_2S	Used portable potentiometer. Granular crystals in bottom of melt. Diff. structure above
18	86.0	907	699–668	FeS + Na_2S	Large crystals in center and on top of melt
12	81.6	850	699–673	FeS + Na_2S	Used portable potentiometer. Similar structure to top of 11. Crystals in center
13	70.3	701	660–647	Run 12 melt + Na_2S	Top of melt cracked and showing long narrow crystals perhaps 1″ by $^1/_{16}$″
17	64.9	696	665–656	Run 16 melt + FeS	Few crystals
14	60.7	695	638–613	Run 13 melt + Na_2S	....
15	50.6	...	625–549	Run 14 melt + Na_2S	Greenish with crystals in center
16	40.7	653	588–560	Run 15 melt + Na_2S	Greenish black with well formed needles in top centers
19	None	970		Na_2S	....

In addition to our own work, three other points in this system have been reported by F. Thomas,[8] but he has placed an erroneous interpretation on his meager data. His points are shown by crosses in circles in our phase diagram, Fig. 2.

In all cases the mixtures wetted the graphite crucibles and the greater the percentage of sodium sulfide the greater the apparent wetting. The only ocular evidences of segregation in the melts are mentioned in the column of "Remarks" in Table I.

The analyses of the samples from the various melts are indicated in Table II. No difficulty was encountered in analysis of the pure iron sulfide samples, but in all cases where sodium sulfide was present more or less graphite was present from the walls of the crucibles and it was not evenly distributed. Even quadruplicate determinations did not check well until chunks of the melts were rapidly pulverized in a porcelain mortar and screened through a 10-mesh sieve to remove coarse pieces of graphite. There are considerable differences between the analyses expected and those

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[8] Thomas, *Metallurgie*, 7, 706 (1910).

TABLE II

ANALYSES OF SAMPLES

Run	Theoretical analysis FeS, %	Na₂S, %	Fe, %	Na, %	S, %	Analysis found Fe, %	S, %	Na, %	Total	
9	100	..	63.54	..	36.46	62.60	37.44	..	100.04	
7	100	..	63.54	..	36.46	62.84	36.92	..	99.95	(Insol. = 0.19)
10	93.5	6.5	59.4	3.8	36.8	56.3	37.1	5.1	98.5	
11	86.4	13.6	54.9	8.0	37.1	55.6	38.4	5.2	99.2	
18	86.0	14.0	54.6	8.2	37.2	49.7	37.7	13.1	100 5	
12	81.6	18.4	51.8	10.8	37.4	48.5	37.5	14.4	100.4	
17	64.9	35.1	41.2	20.7	38.1	39.8	38.2	22.0	100.0	
15	50.6	49.4	32.1	29.1	38.8	31.6	39.0	29.6	100.2	
16	40.7	59.3	25.9	34.9	39.2	23.8	38.5	36.8	99 1	

actually found in several of the samples. In addition to the difficulty due to suspended graphite, there was probably also inhomogeneity due to segregation during cooling and a certain amount of unavoidable oxidation of sodium sulfide to sulfate. Calculating the iron and sodium to sulfide

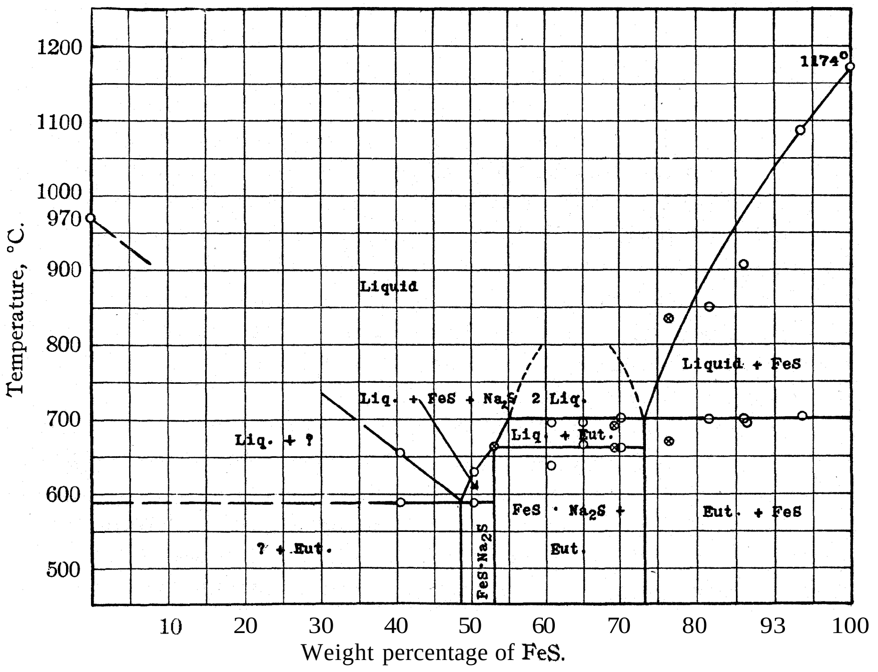

Fig. 2.—The system FeS–Na₂S. ⊗, Thomas; ○, Authors.

in these analyses, there is a slight excess of sulfur remaining in all cases, reaching a maximum of 2.8% in Run 11, but usually much less than this. Due to all these possible sources of error, the "observed" analyses were not used in preparing the phase diagram.

Every melt containing sodium sulfide oxidized rapidly if left in air and an odor of hydrogen sulfide arose from the action of moisture. They would crumble to a powder in a short time if left in the open air. All samples were therefore preserved in sealed containers. Contrary to expectation, the melts which reacted with air most quickly were those containing the higher percentages of iron sulfide.

Phase Diagram.—Based largely on the cooling curves and the ratios of iron sulfide and sodium sulfide used, the phase diagram of Fig. 2 was sketched, giving the temperature–composition relationships as far as it was possible to judge them from the few data. To a certain extent this diagram is supported by the metallographic examination of polished sections which is described below. The liquidus of this diagram is fairly well determined, although melts between pure sodium sulfide and 38% iron sulfide were not prepared and the vacant part of the diagram may be more complex than that sketched. The research was financed mainly to determine the liquidus and much work beyond this objective was not justified.

The secondary arrests in the cooling curves were somewhat difficult of interpretation but it is believed the diagram satisfactorily accounts for them. A separation into two conjugate liquids in the region between 55 and 73% of iron sulfide is necessary, although no direct evidence of this was obtained. Furthermore, the formation of a transitory double compound, $Na_2S\cdot FeS$, is assumed in this area of the diagram. The physical evidence supporting this latter conclusion is the presence of a white constituent in the polished surfaces under the microscope, whereas pure iron sulfide is yellowish and is found in the specimens with greater than 73% of iron sulfide. The composition of the white constituent was not determined but is assumed to be a double compound, probably $Na_2S\cdot FeS$, which seems to fit the cooling curves best.

The exact composition of the transitory double compound, while we believe it to be $Na_2S\cdot FeS$, is insufficiently determined. Stromeyer[9] once prepared what he thought to be $Na_2S\cdot 2FeS$ and it is this double compound which Thorpe[10] assumes caused difficulty in the Blythe and Kopp process of making soda. One of Thomas' points is at the composition $Na_2S\cdot FeS$ and shows only one arrest. He may or may not have missed the eutectic arrest at 585°. Therefore further work in the "two liquids" region of the diagram is urgently needed.

Our interpretation of these meager data is somewhat influenced by the work of F. Friedrich[11] on the system $Na_2S:Ni_3S_2$, which is very similar as far as the form of the phase diagram is concerned.

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[9] Stromeyer, *Ann.*, 107, **233** (1858).

[10] Thorpe, "Dictionary of Applied Chemistry," 1926, Vol. 6, p. 179.

[11] F. Friedrich, *Metall und Erz*, 11, 197 (1914).

Metallographic Examination.—Lumps of about one inch diameter were used for preparation of polished surfaces. To protect them from attack by the atmosphere they were soaked in molten paraffin wax, which was adequate for the period of time necessary in polishing a surface, examining it under the microscope and photographing it. In place of water, kerosene was used on the polishing wheels. The polished surfaces, on account of difficulty of manipulation, are far from perfect, so caution must be used in implying inconsistences between the phase diagram and the micro-structure.

In general the melts high in iron sulfide showed the characteristic yellow iron sulfide dendrites. As melts lower in iron sulfide were approached, the yellow color diminished and in the two-liquid region the crystals seemed to be white. While magnifications up to 1000 diameters were used, a definite eutectic structure was usually difficult to find and especially the temporary eutectic (B) was disappointing from this standpoint.

The notes on the polished sections prepared are given herewith and also four photomicrographs to accompany them.

Examination of Polished Sections

Melt **No.** 10 (**91.1% of FeS**) (Plate I).—Structure consists of rounded grains of yellow iron sulfide in transparent matrix which appears dark under the microscope.

Melt **No. 11** (**90% of FeS**).—The iron sulfide is in the form of long dendrites in the transparent matrix. The dendrites can be seen with the naked eye.

Melt **No. 18** (**78.3% of FeS**).—Similar to No. 10. Irregular patches of yellow iron sulfide, although some are white.

Melt **No. 12** (**76.4% of FeS**) (Plate 2).—Dendrites of iron sulfide in dark matrix. The iron sulfide is much lighter in color than in previous specimens. The iron sulfide areas are much smaller and are very irregular.

Melt **No. 17** (**62.7% of FeS**) (Plate 3).—Small white crystals in the form of squares and triangles in a brown colored matrix which shows no sign of a eutectic structure.

Melt **No.** 15 (50% **of FeS**) (Plate 4).—Tiny specks of the white constituent of previous specimen in groundmass of very coarse eutectic. The groundmass, as can be seen from the photograph, is entirely different from that of the previous specimen.

Melt **No. 16** (37.5% of **FeS**).—Two constituents are present; both are dark by reflected light so that structure cannot be distinguished. Under the binocular microscope it is barely possible to distinguish between them on account of a slight relief due to difference in hardness. One constituent is more sectile than the other and shows a slightly metallic streak when scratched. The absence of eutectic may be due to smearing of the soft constituent when polishing.

Polished sections of Melts 10 and 17 were examined at the highest magnification of which our apparatus is capable (1000 diameters). Both appear to have the same groundmass, which may be a very fine-grained eutectic, but the structure is beyond the resolving power of the apparatus, so that a definite conclusion is impossible. No light colored constituent could be distinguished in the groundmass of either constituent.

Plate 1.—91.1% of FeS. Mag. × 85.

Plate 2.—76.4% of FeS. Mag. × 35.

Plate 3.—62.7% of FeS. Mag. × 170.

Plate 4.—49.8% of FeS. Mag. × 35.

Summary

Eleven melts and cooling curves have been prepared in the system Na_2S–FeS which have allowed preparation of a satisfactory liquidus in the temperature–composition phase diagram but insufficient points were taken to determine fully the solidus and a complete outline of the phase diagram. Such points as have been obtained indicate a region between 53 and 73% iron sulfide in which two liquid phases can form, one being a double compound, probably $FeS \cdot Na_2S$, saturated with iron sulfide, and the other being iron sulfide saturated with double compound, or something similar to it. One true eutectic is found at 46% of iron sulfide and 585°. The melting point of sodium sulfide has been determined as 970°, although its purity was such that the melting point of pure sodium sulfide can be expected to be slightly higher. No mixture containing less than 37% of iron sulfide was investigated.

CLARKDALE, ARIZONA

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

EQUILIBRIUM IN THE SYSTEM $Co–H_2O–CoO–H_2$. FREE ENERGY CHANGES FOR THE REACTION $CoO + H_2 = Co + H_2O$ AND THE REACTION $Co + {}^1/_2O_2 = CoO$

BY P. H. EMMETT AND J. F. SHULTZ

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Introduction

In the course of some experiments with cobalt catalysts, we desired to know the ratio of steam to hydrogen above which cobalt is oxidized to cobaltous oxide. The only determinations in the literature seemed to be those of Chaudron[1] and of Wohler and Balz.[2] The former obtained a value of 20 at 1000°. The latter workers obtained a value of 14 at 450° and 19 at 750°. The apparatus and method of procedure used in both of these researches, however, were those used by Deville[3] in the study of iron oxide equilibria. Such a procedure is not well adapted to the determination of the equilibrium constant in the case of cobalt, since the partial pressure of hydrogen in equilibrium with 25 mm. of water vapor will be a millimeter or less. Any occluded gases in the solid material would cause one to obtain too low a value for the steam–hydrogen ratio. It was, therefore, probable that one or both of the above experiments might be in error, especially since preliminary observations indicated that the equilibrium ratio of steam to hydrogen was 50 or greater at 450°.

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[1] Chaudron, **Ann.** *chim.*, **16,243 (1921).**

[2] Wohler and Balz, *Z.* ***Elektrochem.***, 27, ***406*** **(1921).**

[3] Sainte-Claire Deville, ***Compt.*** rend., 70, ***834*** **(1870).**

Accordingly, the present work was undertaken with a view to determining accurately, at several different temperatures, the equilibrium ratio of water vapor to hydrogen for the reaction $CoO + H_2 = Co + H_2O$. This paper outlines the essential details of procedure, and presents typical equilibrium data for 335, 450, 515 and 570°.

Apparatus and Materials

For the equilibrium determinations a flow system has been employed, similar in most respects to that used by Pease and Cook[4] in their investigation of the system $NiO–H_2–Ni–H_2O$. The apparatus as finally adopted is shown in Fig. 1. It consists essentially of a steam generator A, an electrolytic hydrogen generator B, a pyrex glass tube C containing the charge, an electric furnace D, a water-jacketed weighing tube E for catching and weighing the condensed steam and a special 100-cc. eudiometer F for measuring the hydrogen. The steam boiler used is similar to the one described by Kuentzel,[5] except that the steam exit has been so modified as to reduce the probability of tiny droplets of liquid water being carried over with the steam. The hydrogen cell was fitted with platinum electrodes and contained potassium hydroxide as an electrolyte. The hydrogen was purified by passage over soda lime and hot platinized asbestos. The tube containing the charge was heated in a furnace 48-cm. long, consisting of an alundum tube wound with nichrome ribbon embedded in magnesia and finally surrounded by an iron jacket. The bulb containing the charge was placed in the alundum tube and packed tightly with mossy copper. Temperature was measured by means of an alumel-chromel thermocouple in conjunction with a Leeds and Northrup portable potentiometer. It was found to remain constant within ±1° during a run.

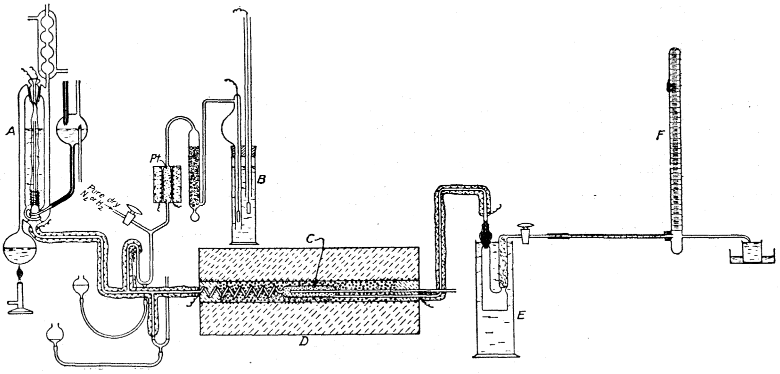

Fig. 1.—Apparatus.

The temperature gradient along the length of the catalyst was found to be less than 2°. It was obtained by moving a thermocouple along the thermocouple well extending coaxially along the entire catalyst tube. In several of the experiments an auxiliary thermocouple was placed in contact with the outside wall of the catalyst container. It showed the transverse temperature gradient to be less than 2° for half the width of the catalyst tube.

The flow of gases through the apparatus was regulated by mercury cut-offs rather than by dry stopcocks, since the latter when used are inclined to leak. The mercury

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[4] Pease and Cook, THIS JOURNAL, 48, 1199 (1926).

[5] Kuentzel, unpublished material.

in the cut-offs was always covered with a centimeter or more of water and hence did not come directly in contact with any heated portion of the tubes. The top of the steam generator was water-sealed during all runs in order to preclude any possibility of air diffusing into the apparatus. The lead wires to the hydrogen generator were welded to tungsten which in turn was sealed through the pyrex glass of the generator.

Two different cobalt oxide preparations were used in the present experiments. Catalyst No. 1 was prepared by fusing a sample of nickel-free metallic cobalt with an oxyhydrogen flame in a crucible of cobalt coated with cobaltous oxide. Excess oxygen was blown into the melt during the fusion. The resulting oxide analyzed very nearly pure cobaltous oxide. It was used in the form of 10- to 14-mesh materiai.

Catalyst No. 2 was prepared by first gently and finally strongly igniting a sample of C. P. recrystallized cobaltous nitrate. The first gentle heating was in an open porcelain dish. The final higher heating to approximately 500° was of several hours duration and took place in a glass tube with a stream of air passing continually. The apparent density[6] of catalyst No. 1 was 2.65, and of No. 2, 0.76. The composition of this latter material was very nearly Co_3O_4. It accordingly had to be reduced for some hours with a steam–hydrogen mixture in which the ratio of steam to hydrogen was slightly too high to permit the reduction of the CoO formed. By such procedure a pure CoO was obtained.

Experimental Procedure

The reaction tube filled with 20 to 25 cc. of one of the cobalt oxides was packed into the furnace, connected to the steam and hydrogen generators and brought to the desired temperature in a slow stream of oxygen-free nitrogen. After being suitably reduced by hydrogen, the catalyst was subjected to various definite steam–hydrogen mixtures and the effluent gases were analyzed for water and hydrogen. The inlet and exit steam–hydrogen ratios were determined by three measurements: (1) the weight of exit steam condensed in the water jacketed U-tube in a given time; (2) the volume of exit hydrogen (corrected to S. T. P.) collected during the same period of time; and (3) the current passed through the hydrogen cell during the run. The effluent hydrogen, in addition to being corrected to S. T. P. on a dry basis in the usual way, had also to be corrected first for the volume of the gas displaced into the measuring buret by the condensation of steam in the U-tube, and second for the volume forced out of the U-tube by slight heating resulting from the rapid flow of steam. The first of these two corrections was, of course, easily and accurately made. The second was also definitely determined by using as the inlet tube to the eudiometer F a pipet stem graduated in 0.1 cc. divisions and easily readable to 0.01 cc. Immediately on shutting off the steam flow at the end of a run, the water from the eudiometer quickly sucked back into the pipet entrance tube as the heated portions of the U-tube rapidly cooled. This heating correction was usually of the order of **0.3** cc. It was very constant and easily obtained under a given set of conditions.

Experiments in general were repeated many times at each particular temperature, using first, Catalyst No. 1 and then Catalyst No. 2. Equilibrium was approached at each temperature from both the steam and the hydrogen sides.

Experimental Results

In order to obtain approximate values for the equilibrium constant and to learn how rapidly equilibrium could be attained, numerous preliminary experiments were carried out over a temperature range of **335**

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[6] By "apparent density" of a sample is here meant its weight in grams divided by its approximate apparent volume as measured in a graduated cylinder.

to 515°. During these runs 6 or 7 different types of apparatus were tried. By a process of elimination the poor features of different analytical devices were remedied and eventually the final apparatus described in Fig. 1 was obtained.

In the three hundred or more preliminary runs it became apparent that the material was often not very active, particularly at 335°. Even at 450° considerable trouble was experienced in getting sufficiently large changes in the exit as compared to entering gas ratios. However, these preliminary results in spite of analytical difficulties give a fair approximation to the equilibrium constants.

TABLE I

PRELIMINARY RUNS AT 335°

	Inlet mixture		Exit totals			
Run no.	Steam, cc./min.	Hz, cc./min.	Water, g.	Hz, cc. (S. T. P.)	H_2O/H_2 In	Out
			50 Grams of Catalyst No. 1			
36	49.3	1	0.469	6.79	49.3	85.9
126	94.2	1	1.006	14.99	94.2	83.5
127	95.7	1	1.032	15.00	95.7	85.6
128	93.5	1	1.023	14.97	93.5	85.0
252	99.3	1	1.212	17.24	99.3	87.4
			14.5 Grams of Catalyst No. 2			
193	67.7	1	0.448	7.03	67.7	79.3
196	94.5	1	.473	6.76	94.5	87.0

From the results, part of which are shown in Table I, it is believed that the equilibrium constant at 335° is 85 ± 5. Due to the slowness with which a gas mixture attained equilibrium over the oxide mixtures at this low temperature, no final measurements at 335° were attempted. The 450 and 515° preliminary results are not listed since the final results are much more significant and more closely indicative of the true equilibrium constants. The preliminary results at these temperatures indicated that the value of the constant at 450° would be 65 ± 5, and at 515° would be 53 ± 5.

The final runs were all made using the apparatus as described in Fig. 1. Each experiment was continued until 90 to 100 cc. of effluent hydrogen was collected in the eudiometer. The 450° values are shown in Table II. Herein are included only those final runs in which the exit ratio differs by 5% from the entering and in which the final value is within the range of 63 to 71. None of the omitted values contradicts any of the values in Table II. The single contradiction in the runs at 450° (Run 393) is included in Table II, and is believed to have been caused by some unaccountable experimental error. Furthermore, the first two readings after either a 100% steam treatment or a reduction with pure hydrogen (designated in Tables II and III by *a* and b, respectively) have not been included in the final choosing of the equilibrium constant, in that the former are usually low by about 5 to 10% and the latter high by about the same amount. It is believed from the results obtained that a value of 67 ± 1, represents closely the equilibrium constant of the reaction.

TABLE II

FINAL RUNS AT 450°

	Inlet mixture		Exit totals		H_2O/H_2		
Run no.	Steam, cc./min.	Hz, cc./min.	Water, g.	H_2, cc.	In	Out	Approx. % of metallic cobalt
			70 8 Grams of Catalyst No. 1				
369	122.7	2	4.564	83.22	61.4	68.3	7
361	1050	2	4872	83.03	525	73.0"	7
364	86.8	2	4.722	83.81	43.4	70.1	7
382	142 8	2	4.560	83.42	71.4	67.9	61
			23.8 Grams of Catalyst No. 2				
393	187.6	4	2.914	84.53	46.9	42.9	23
397	211.8	3	4.489	8328	706	67.0	9
398	183.6	3	4.236	53.68	61 2	63.7	9
410	155.4	2	4.101	85.42	77.7	59.7^b	80
440	177.5	2	4.285	83.65	88.8	63.7^b	76
441	148.5	2	4.505	83.42	74.3	67.2	76
442	1458	2	4.549	83.37	729	67.8	76
443	123.5	2	4.393	83.38	61.8	65.6	76
444	121.5	2	4.272	83.74	60.8	63.5	76

[a] Pure steam was passed over catalyst for thirty minutes or more immediately prior to this run. [b] 200 cc./min. of pure hydrogen was passed over catalyst for five minutes or more immediately prior to this run.

TABLE III

FINAL RUNS AT 515°

	Inlet mixture		Exit totals		H_2O/H_2		
Run no.	Steam, cc./min.	Hz, cc./min.	Water, g.	H_2, cc.	In	Out	Approx. % of metallic cobalt
			70.8 Grams of Catalyst No. 1				
346	125.7	2	4.000	85.17	62.9	58.5	7
347	76.2	2	3.807	83.63	38.1	56.6	7
348	90.1	2	3.804	83.22	45.0	56.9	7
350	139.5	2	3.800	82.84	69.8	57.1	7
366	110.1	2	4.773	83.55	55.1	71.0^a	7
367	77.0	2	3.976	8562	38.5	57.7	7
368	85.0	2	3.953	85.85	42.5	57.3	7
369	150.6	2	3.910	85.62	75.3	56.8	7
370	138.8	2	3.922	85.28	694	57.2	7
371	146.8	2	3.888	85.82	73.4	56.3^b	84
372	141.0	2	3.882	85.83	70.5	56.3	84
373	140.2	2	3.881	85.79	70.1	56.3	84
374	97.8	2	3.815	85.88	48.9	55.3	84
375	128.0	2	3.971	95.14	64.0	58.0^a	61
376	137.7	2	4.158	84.86	68.9	60.9	61
377	118.2	2	3.927	84.68	59.1	57.6	61
378	102.5	2	3.828	84.43	51.2	56.4	61

TABLE III *(Concluded)*

Run no.	Inlet mixture Steam, cc./min.	H_2, cc./min.	Exit totals Water, g.	H_2, cc.	H_2O/H_2 In	Out	Approx. % of metallic cobalt
			23.8 Grams of Catalyst No. 2				
403	155.7	3	3.720	84.01	51.9	55.0	9
404	221.0	3	3.969	83.36	73.3	59.2	9
405	186.5	3	3.928	83.56	62.2	58.4	9
406	163.0	3	3.835	83.60	54.3	57.0	9
407	156.3	3	3.696	83.45	52.1	55.1	9
429	153.5	3	3.758	83.66	51.2	55.9[b]	61
430	193.8	3	3.811	83.57	64.6	56.8	61
431	206.0	3	3.867	83.33	68.6	57.6	61

[a] Pure steam was passed over catalyst for thirty minutes or more immediately prior to this run. [b] 200 cc./min. of pure hydrogen was passed over catalyst for five minutes or more immediately prior to this run.

The values obtained for 515° are given in Table III. All values obtained have been included (excepting 4 values to be listed and explained in connection with Table V) in which the entering and exit ratios differ by 5% or more and the final value lies between 55 and 60. From the data thus obtained, the equilibrium constant for 515° appears to be 57 ± 0.3. At this temperature, too, the results of the first run following treatment with 100% steam or with pure hydrogen are higher or lower, respectively, than the normal equilibrium values and accordingly are not considered in choosing the equilibrium constant.

In Table IV are given the results obtained at a temperature of 570°. Except for one group of 8 runs, reserved for Table V, all of the final 570° experimental values are included. The equilibrium constant at 570° is 50.5 ± 0.2.

TABLE IV

TEMPERATURE, 570°

Run no.	Inlet mixture Steam, cc./min.	H_2, cc./min.	Exit totals Water, g.	H_2, cc.	H_2O/H_2 In	Out	Approx. % of metallic cobalt
			70.8 Grams of Catalyst No. 1				
354	80.0	2	3.428	84.15	40.6	50.7	7
355	124.4	2	3.428	84.55	63.7	50.4	7
356	122.6	2	3.412	84.12	62.8	50.5	7
			23.8 Grams of Catalyst No. 2				
408	130.8	3	3.380	83.59	43.6	50.3	9
409	181.6	3	3.396	83.71	60.5	50.4	9
432	122.1	3	3.374	82.77	40.7	50.7	61
433	122.3	3	3.373	82.95	40.8	50.6	61
434	117.1	3	3.215	82.73	39.0	48.4	61
435	167.3	3	3.372	83.14	53.7	49.9	61
436	181.7	3	3.384	83.18	60.5	50.6	61
437	171.3	3	3.381	82.96	57.1	50.7	61

One group of experiments was carried out to ascertain whether or not the same equilibrium constant prevailed even when the solid phase consisted of a small amount of oxide and a large amount of metal. A definite shift in the equilibrium constant would indicate the formation of solid solutions over a limited range. The results of the twelve runs thus made are shown in Table V.

TABLE V

RESULTS OF EXPERIMENTS

Run no.	Inlet mixture Steam, cc/min.	H_2, cc/min.	Exit totals Water, g.	H_2, cc.	H_2O/H_2 In	Out	Approx. % of metallic cobalt
			Temperature, 515"				
412	97.9	2	3.516	85.15	49.0	51.4	80
413	107.2	2	3.639	85.17	53.6	53.2	80
414	134.8	2	3.687	84.83	67.4	54.0	80
415	123.3	2	3.674	83.86	61.7	54.5	80
			Temperature, 570°				
416	88.9	2	3 220	84.40	44.5	47.5	80
417	121.0	3	3.227	84.44	40.3	47.5	80
418	150.2	3	3.139	84.17	50.1	46.4	80
419	164.3	3	3.179	83.73	54.8	47.2	80
420	185.4	3	3.121	84.58	61.8	45.9	88
421	185.0	3	3.262	84.48	61.3	48.0	88
422	185.6	3	3.352	84.79	61.9	49.3	88
423	187.4	4	3.313	84.47	46.9	48.8	88

Run 412 was made immediately after reducing a sample until it contained only 20% of cobaltous oxide. Just before Run 420, additional reduction dropped the oxide content to approximately 12% of the sample. It was at first thought that the results indicated a definite shift in equilibrium constant. Unfortunately time limitations prevented the obtaining of further data upon this point. If due allowance is made for the already noted tendency of ratios immediately following long reduction to be low, the results in Table V are believed to be explainable without assuming the formation of solid solutions. Particularly, Runs 420, 421 and 422 suggest the probability that the low ratios are the result of the long reduction, for the exit ratio is in these runs definitely increasing toward the 50.5 value, believed to be the true equilibrium constant. Furthermore, as will be seen from the x-ray photographic data given below, no evidence of solid solutions for these samples is furnished by the powder photographs taken.

It should be noted that Runs 429 to 444 shown in Tables II to IV were all taken after those in Table V, the only change being that between Runs 428 and 429 the catalyst was steamed for seventeen hours at 500°. Hence it is certain that the analytical apparatus was operating in the same way before and after the twelve runs of Table V.

From the data presented in Tables I to V, it can be concluded that the equilibrium ratios of steam to hydrogen in contact with the oxide–metal mixture present are as follows:

Temperature, °C.	335	450	515	570
Ratio	85 ± 5	67 ± 1	57 ± 0.3	50.5 ± 0.2

The 335° value is only approximate and was determined in preliminary runs.

It was next necessary to establish definitely that the cobalt oxide in the above experiments was CoO and not Co_3O_4, Co_2O_3 or a solid solution of two of the oxides.

We were fortunate in having facilities available for checking the composition of all the materials used in these determinations by x-ray photograph~.~

In Table VI are listed the samples of which powder photographs were taken as a means of ascertaining definitely the solid phases existing in the equilibria measurements. These photographs were made with MoKα radiation. Since all the substances present in these samples have been previously examined by means of their x-ray powder diffraction patterns, it was not considered necessary to list in detail the results obtained.

TABLE VI

POWDER PHOTOGRAPH RESULTS

	History of sample	Phases revealed by powder photographs
a	Pure CoO (Sample of Catalyst No. 1)	CoO
b	Co_3O_4 (Sample of Catalyst No. 2)	Co_3O_4
c	Catalyst No. 1, 9% reduced at 283°	CoO and hexagonal Co
d	Catalyst No. 1, 75% reduced at 288"	CoO and hexagonal Co
e	Mixture of Sample c and CoO	CoO (no line displacement) and hexagonal Co
f	Mixture of Sample d and CoO	Same as in e
g	Final material remaining after Run 444 in the equilibrium measurements	Cubic Co and CoO
h	Sample obtained by steaming a completely reduced Co_3O_4 sample for eight hours at 500° with rapid flow of steam. During this time the sample was 70% reoxidized, as detd. by hydrogen formed	Cubic Co and CoO
i	Sample prepared by passing a mixture containing steam and hydrogen in the ratio of 70 to 1 over a sample of Co_3O_4 at 500° for ten hours	Strong CoO Faint Co_3O_4
j	Co_3O_4 reduced at 310°	Hexagonal Co
k	Co_3O_4 reduced at 340°	Hexagonal Co
l	Co_3O_4 reduced at 383°	Cubic cobalt
m	Co_3O_4 reduced at 360°	Cubic and hexagonal cobalt

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[7] For these powder photographs and their interpretation we are indebted to Dr. S. B. Hendricks of this Laboratory. We wish to express our appreciation for his cooperation.

Substances identified by the powder lines on the photograph are indicated in the table.

With the exception of Samples a and b, all the materials listed in the above table were examined without allowing them to come in contact with the atmosphere.

These photographic results we believe enable us to conclude (1) that cobaltous oxide and cobalt were the only solid phases present during the equilibrium measurements; (2) that no evidence for the existence of a solid solution between cobaltous oxide and cobalt under the conditions of these experiments can be found in the powder photographs obtained.

In view of the above facts, it seems justifiable to conclude that the equilibrium results summarized above apply to the equilibrium Co–CoO–H_2O–H_2.

The results summarized under j, k, 1 and m were taken by Dr. Hendricks in order to fix the transition temperature of cobalt. It has previously been known that cobalt obtained by reduction of the oxide at 600°, has a "face-centered" cubic structure while that usually present in cast cobalt has a "close-packed" hexagonal structure. The transition temperature was not even approximately known nor could it be determined by the usual method of thermal analysis, since the rate of transformation of one form to another is very sluggish at 300–400°. From the information listed in Table VI, it can be concluded that the transition temperature is between 340 and 360°.

It should be noted in the results in Tables I, II, III, IV and V that values for the effluent ratio of steam to hydrogen are higher than normal immediately after oxidation and lower immediately after reduction. Such runs are. designated by *a* and b, respectively, as described in Table II. This is analogous to the effect mentioned by Richardson, Vibrans and Bell[8] for iron oxide reduction, and by Pease and Cook[4] in the case of the equilibrium determination of hydrogen-steam ratio over Ni–NiO mixtures. A similar phenomenon is reported for metallic iron catalyst by Almquist and Black.[9] In this latter case the circulation over an iron catalyst of a 3:1 hydrogen–nitrogen mixture containing from 0.008 to 0.32% of water vapor was found to form small but definite amounts of oxide upon the surface of the iron. This oxide has been interpreted by Almquist[10] as being due to the oxidation of surface atoms having free energies of the order of 10,000 calories greater than that of normal surface iron atoms. Eastman and Evans[11] have noted the tendency of the equilibrium hydrogen–steam ratio over Fe–FeO to increase as the

[8] Richardson, Vibrans and Bell, *Science*, **56**, 27 (1922).

[9] Almquist and Black, THIS JOURNAL, 48, 2814 (1926).

[10] Almquist, *ibid.*, 48, 2820 (1926).

[11] Eastman and Evans, *ibid.*, 46, 888 (1924).

oxygen content of the solid phases decreased, and have mentioned it as being indicative of a solid solution existing between iron and ferrous oxide. This phenomenon, however, quite probably is distinct from the one noted by Almquist and Black in that it was obtained under conditions making solid solution much more likely than in the case of their experiments. In the present work the values marked with a a or b in Tables II, III and IV are of such magnitude and obtained under such conditions as probably to be due to a surface effect rather than to the formation of a solid solution. Furthermore, as already pointed out, powder photographs reveal no shifting of lines of cobaltous oxide containing small amounts of cobalt or cobalt containing small amounts of cobaltous oxide, making the existence of solid solutions between these solid phases improbable.

One difference between the above-mentioned effect on nickelous oxide as reported by Pease and Cook and on cobaltous oxide as recorded in the present work should be noted. The former authors give data showing a rather high hydrogen consumption by nickelous oxide on passage of a steam–hydrogen mixture. Thus, one 84-g. sample of NiO when treated with 150 cc. per minute of a 150–1 steam–hydrogen mixture permitted no hydrogen to pass during the first twenty hours. Had the exit gases contained the normal equilibrium hydrogen some 554 cc. of hydrogen would have been collected during this time. Accordingly, hydrogen equivalent to about 2.1% of the oxygen of nickelous oxide was consumed before any appeared in the effluent gas. In contrast to this, the cobaltous oxide samples of the present work never absorbed more than a few cc. of hydrogen when similarly treated. The very first reading usually differed from the true equilibrium value by only 5 or 10%. Complete equilibrium usually resulted within an hour of the first passage of steam–hydrogen over the oxide. This excessive consumption of hydrogen by nickelous oxide as compared to cobaltous oxide may indicate an unusually large surface effect by the nickelous oxide preparation as compared to the cobaltous oxide. On the other hand, it may in part at least be due to the consumption of some hydrogen by small amounts of Ni_2O_3 present in the NiO. This possibility would necessitate that the oxide be of the empirical composition $NiO_{1.021}$ approximately. The highest percentage of oxygen reported by Pease and Cook was 21.8% in contrast to the 21.43% theoretically needed for NiO. This corresponds to a composition of $NiO_{1.018}$. Furthermore, Benton and Emmett[12] reported certain samples of NiO which were prepared by ignition of the nitrate in air at 360 to 400° for many hours to have a composition as rich in oxygen as $NiO_{1.032}$. Accordingly, it does not seem unreasonable that part of the effect reported by Pease and Cook was in reality due to the reduction of small amounts of one of the higher oxides of nickel. Hence, in nickelous oxide the true "surface" effect

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[12] Benton and Emmett, THIS JOURNAL, 46,2728 (1624).

causing hydrogen from a steam–hydrogen mixture in contact with pure metal to be consumed in excess of equilibrium requirements may not be different from that found for cobaltous oxide.

Free Energy Calculations.—From the equilibrium data obtained in the present investigation, the standard free energy and heat content changes for the reaction

$$CoO + H_2 = Co + H_2O \qquad (1)$$

can easily be calculated. Inserting the values 67, 57.0 and 50.5 for K at 723, 788 and 843°, respectively, into the equation[13]

$$\Delta F^\circ = -RT \ln K$$

one readily obtains ΔF°_{723}, ΔF°_{788} and ΔF°_{843}, as −6045, −6335 and −6574 calories, respectively. In the absence of specific heat data for cobaltous oxide, we have used a value of 10, obtained by Kopp's law as outlined in Noyes and Sherrill[14] and for cobalt a value of 6. These specific heat values, together with those for water vapor and hydrogen given by Lewis and Randall, yield a ΔC_p value of $-1.69 - 0.0028T + 0.00000222T^2$. Inserting ΔF° values for the three temperatures given above in the equation

$$\Delta F^\circ = \Delta H_0 - \Delta\Gamma_0 T \ln T - {}^1/_2\Delta\Gamma_1 T^2 - {}^1/_6\Delta\Gamma_2 T^3 \ldots\ldots + IT$$

and solving the three sets of resulting equations for I, values of −18.91, −18.83 and −18.87 are obtained. Using an average **I** value, an average ΔH_0 value of −1040 calories is obtained. Whence $\Delta H_{298} = -1646$ calories, and $\Delta F^\circ_{298} = -3678$ calories for Reaction 1 above.

In Fig. 2 the smooth curve represents a plot of $1/T$ against the logarithm of the equilibrium constant as calculated for temperatures between 335 and 1050° from the ΔF° equation given above, using for ΔH_0 −1040 calories, for **I** a value of −15.87 and for ΔC_p the expression $-1.69 - 0.0028T + 0.00000222T^2$. It is realized that the high temperature extrapolation of our own values hereby obtained is uncertain because of the assumptions as to the specific heats of cobalt and cobalt oxide. More dependable extrapolations to the higher temperatures must await specific heat data on cobaltous oxide. From the figure, assuming the above extrapolation to be approximately correct, we conclude that our own data are consistent with the value of 20 ± 10, obtained by Chaudron, for the constants at 1050°. The results of Wohler and Balz, however, are much lower than our own. It is tempting to suggest that the value 34 reported by them to be the constant for the oxidation of CoO to Co_3O_4 by steam may actually have been obtained when CoO and Co were present and may accordingly refer to the equilibrium measured in the present research.

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[13] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

[14] Noyes and Sherrill, "Chemical Principles," The Macmillan Co., New York, **1928**, **p. 93.**

By combining the free energy for Reaction 1 with that[13] for the reaction

$$H_2O = H_2 + {}^1/_2O_2 \qquad (2)$$

one obtains the ΔF°_{1373} for the reaction

$$CoO = Co + {}^1/_2O_2 \qquad (3)$$

as +32,050 calories. By the equation $\Delta F^{\circ} = -RT \ln K$, the dissociation pressure of the oxide at 1373° is given as 0.5×10^{-7} mm. This value is consistent with the experiments of Foote and Smith[15] in which the dissociation pressure of cobaltous oxide was too small to be measurable at 1373°.

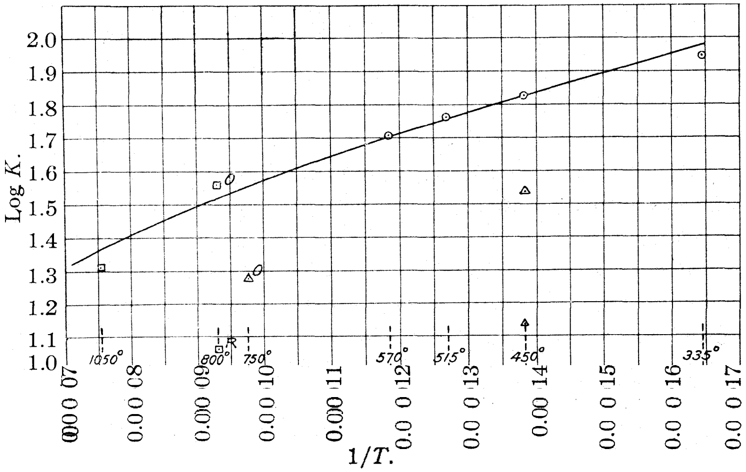

Fig. 2.—⊙, Emmett and Shultz; ⊡, Chaudron; △, Wohler and Balz.

Experimental ΔH values of Mixter[16] for Reaction 3 above are 57,587 calories for crystalline CoO and 50,180 calories for "amorphous" cobalt oxide. The so-called "amorphous" values were obtained by the indirect oxidation of cobalt by means of sodium peroxide rather than the direct oxidation with gaseous oxygen used in determining the 57,587 value. It is quite probable, accordingly, that this difference in procedure rather than the difference in fineness of subdivision of the final product causes the discrepancy between the two values for the heat of oxidation of cobalt to cobaltous oxide.

It is interesting to calculate indirectly from our own data the ΔH value for Reaction 3. By combining the ΔH_{298} value obtained above for Reaction 1 and the well known ΔH_{298} value for Reaction 2, one obtains $-1646 + 57{,}800 = 56{,}154$ calories as ΔH_{298} for Reaction 3. This compares favorably with Mixter's value of 57,587 calories.

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[15] Foote and Smith, **This Journal**, 30, 1349 (1908).

[16] Mixter, *Am. J. Sci.*, 30, 193 (1910).

As confirmation of the fact that no Co_3O_4 was obtained by passage of steam over CoO, a combination of the ΔF° value for the reaction

$$Co_3O_4 = 3CoO + {}^1/_2O_2 \qquad (4)$$

as calculated from the dissociation pressure of (4) given by Foote and Smith[15] and Reaction 2, above, yields ΔF°_{603}, ΔF°_{788} and ΔF°_{1073} values for the reaction

$$Co_3O_4 + H_2 = 3CoO + H_2O \qquad (5)$$

of −34,197, −36,539 and −44,717 calories, respectively. Corresponding ratios of steam to hydrogen necessary to produce oxidation of the CoO to Co_3O_4 are 2.4×10^{12}, 1.3×10^{10} and 1.3×10^{9}. Hence, no formation of Co_3O_4 under the conditions of the above experiments would be expected.

This conclusion is in agreement with our own experimental values but is in direct contradiction to the results of Wohler and Balz,[2] who reported a value of 34 for the above ratio at a temperature of 450°.

In the above calculations nothing has been said about the possible free energy change involved in the transformation from hexagonal to cubic cobalt. All experiments except those at 335° were carried out in the temperature region in which the cubic modification of cobalt is the stable one. In the absence of the necessary data no correction has been made for any free energy change involved in the transformation from hexagonal to cubic cobalt.

Summary

1. The ratios of steam to hydrogen in equilibrium with a mixture of cobalt and cobaltous oxide have been determined by a flow method. The values obtained for this ratio are 67 ± 1, 57.0 ± 0.3 and 50.5 ± 0.2 at 450, 515 and 570°, respectively. An approximate value of 85 ± 5 has been obtained at 335°.

2. ΔF°_{298} for the reaction $CoO + H_2 = H_2O + Co$ has been calculated as −3678 calories.

3. The calculated value of ΔH_{298}, −1646 calories, for the above reaction is to be compared with a value, −300 cal., obtained by the combination of Mixter's experimental heat of formation of cobaltous oxide and the well-known heat of formation of water.

4. The failure of steam passage over CoO at 500° to form Co_3O_4 has been verified by x-ray photographs. A calculated value has been obtained for the theoretical steam–hydrogen ratio necessary to effect such an oxidation. This was obtained by a combination of the dissociation pressure measurements of Co_3O_4 made by Foote and Smith, and the value for the ΔF° change involved in the formation of water from hydrogen and oxygen. It is believed that the calculated value is approximately correct and accordingly confirms the impossibility of any appreciable amount of Co_3O_4 having been formed by passage of steam–hydrogen

mixture over cobaltous oxide in the temperature range of 330 to 570° in the above experiments.

5. ΔF°_{1373} for the formation of cobaltous oxide from cobalt and oxygen has been calculated by combining the free energy change involved in forming water vapor from hydrogen and oxygen with that found experimentally in the present research for the reduction of cobaltous oxide to cobalt by hydrogen. A value of 32,030 calories so obtained yields a value of 0.5×10^{-7} mm. for the partial pressure of oxygen in equilibrium with CoO–Co mixture at 1100°, that is, in agreement with Foote and Smith's failure to detect measurable dissociation of cobaltous oxide at that temperature.

6. The temperature of transformation of hexagonal to cubic cobalt has been fixed as lying between 340 and 360°.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

AN APPARATUS FOR TESTING DÜHRING'S LAW FOR CORRESPONDING BOILING POINTS

BY ERWIN F. LINHORST

RECEIVED JUNE 3, 1929 PUBLISHED NOVEMBER 8, 1929

Introduction

In 1577 Dühring[1] found that a linear relation existed between the boiling temperatures of two liquids boiling under the same pressures. So far this law has been tested indirectly by plotting corresponding boiling points from vapor-pressure data obtained for the two liquids separately. If the two liquids could be boiled in different parts of a closed system, then as the pressure is varied in the system, the corresponding boiling temperatures could be observed directly. This was tried out and it has given satisfactory results. The apparatus is of simple construction and is easy to manipulate.

Discussion

The apparatus is illustrated in Fig. 1. Bulbs are blown at the bottom of two upright reflux Liebig condensers. At the top the condensers are connected to each other and to a vacuum pump, which may be an ordinary aspirator. In the latter case a water trap should be provided in the evacuating train. In order to condense the vapors of the boiling liquids at low temperatures ice water should be led through the condensers.

The liquids to be boiled are poured into the bulbs to about the level indicated in the figure. Porous plate or bisque fragments are added to minimize bumping. The boiling temperatures are obtained by two

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[1] Dühring, *Wied. Ann.*, **11**, **163** (1880).

thermometers entering the bulbs through necks on the bulbs. Airtightness is secured by pieces of rubber tubing fitting over the thermometers and the necks. A cloth gasket is desirable in the case of an organic liquid in order to minimize contact of the liquid with the rubber.

The heating may be done by small flames of Bunsen burners. The bulbs containing the liquids are shielded by asbestos sheets having small holes in the center to permit local concentrated heating and thus help to reduce bumping.

In actual operation it is best to evacuate first and start the liquids boiling at low temperatures and to let a slow leak into the apparatus gradually raise the boiling temperatures. Another advantage of starting at low temperatures is that the liquids are then most likely to bump, but the pores of the porous plate contain then more air than later and are thus more effective in reducing bumping. The air leak may be controlled by a screw clamp over a rubber tubing on the exhaust tube. The temperatures may be read conveniently at degree intervals. A continuous rise in temperature of 1° in three to five minutes is found to be slow enough for accuracy. When the pressure is back to atmospheric, it may be carried a little above by admitting compressed air at low enough pressure so as not to endanger the apparatus.

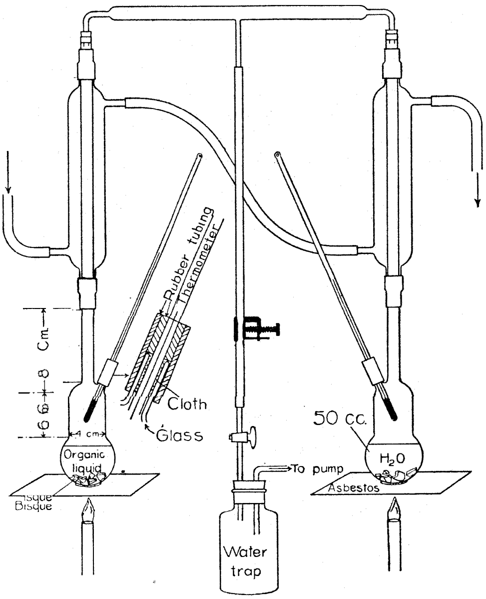

Fig. 1.

The observed temperatures have to be corrected for the length of the mercury thread exposed to room temperature. This correction is to be added to the reading of the thermometer. It is expressed by the formula

$$C = 0.00016 \times l_{\mathrm{Hg}} (t - t_{\mathrm{R}})$$

where l_{Hg} is the length of the exposed mercury column in degrees, t is the reading of the thermometer and t_{R} is the room temperature.

The apparatus was tried out for benzene and ethyl alcohol against water. The equation of the corresponding boiling-point curve for alcohol was found to be

$$t_{\mathrm{A}} = -12.23 + 0.9062\, t_{\mathrm{W}} \tag{1}$$

The maximum deviation of observed readings from this relation was less than 0.07' in absolute value and nowhere was there a trend toward either algebraic sign of the deviations. The boiling temperature at one atmosphere calculated from the equation is 78.39'. The value given in "International Critical Tables," Vol. III, p. 217, is 78.32°.

The results obtained for benzene do not follow a single linear relation so well; they form a curve slightly concave upward. The data may, however, be represented closely by three line segments, each holding for part of the curve. From 54 to 70° on the water axis the line

$$t_B = -30.49 + 1.0948\, t_W \tag{2}$$

holds, from 70 to 90° the line

$$t_B = -32.39 + 1.1222\, t_W \tag{3}$$

and from 90 to 105' the line

$$t_B = -34.77 + 1.1491\, t_W \tag{4}$$

The maximum deviations of observed values from these lines was less than 0.08' in absolute value. The boiling point of benzene at one atmosphere therefore is 80.14". Smith and Menzies[2] found it to be 80.12'. Both the benzene and alcohol were of high purity and were used for molecular weight determinations. The experiment for the benzene was repeated with another sample and practically the same results were obtained.

Figure 2 represents the data graphically. In Table I are shown some vapor-pressure values of alcohol and benzene as calculated from Equations 1, 2, 3 and 4 and a reliable table of the vapor pressure of water. The corresponding values found by others are also given in the table for comparison.

TABLE I

RESULTS

	Vapor pressure in mm. of mercury			
	Alcohol		Benzene	
Temp., °C.	Calcd.	Crit. tables[a]	Calcd.	Stnith and Menzies (Ref. 2)
35	102.7	103.7	148.14	
40	135.2	135.3	182.5	
45	172.5	174.0	223.3	
50	220.6	222.2	270.5	
55	279.5	280.6	325.6	
60	352.4	352.7	390.1	...
65	437.5	438.8	464.9	463
70	540.7	542.5	549.7	551
75	664.0	666.1	646.3	650
80	809.5	812.6	756.7	757.5
85	981.0	986.3	...	

[a] "International Critical Tables," Vol. III, p. 217.

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[2] Smith and Menzies, THIS JOURNAL, 32,1448 (1910).

Any inherent errors in the apparatus are present in both halves, and if the two temperatures are close together, these errors largely cancel each other. To make this more certain the two halves of the apparatus should be as nearly alike as possible. High-grade thermometers of the same type should be used.

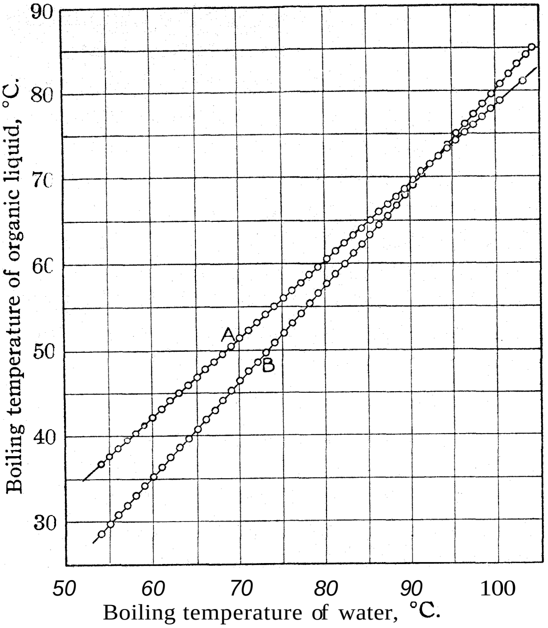

Fig. 2.—A, Ethyl alcohol; B, benzene.

This apparatus as shown is applicable only to pure liquids, where the vapor has the same chemical composition as the liquid, not to solutions or mixtures, where this is not in general, true.

Summary

An apparatus was developed for testing Dühring's law of corresponding boiling points. It was tried out for benzene and ethyl alcohol. The law was found to hold for the alcohol over the range observed but not for the benzene.

Ann Arbor, Michigan

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

PH MEASUREMENT WITH THE GLASS ELECTRODE AND VACUUM TUBE POTENTIOMETER

BY L. W. ELDER, JR.

RECEIVED JUNE 7, 1929 PUBLISHED NOVEMBER 8, 1929

In a previous communication a single tube vacuum tube potentiometer was described which gave satisfactory potential readings in acid and alkali when a suitable glass was used.[1,2] The present paper deals with a further modification of this apparatus and presents the results of a direct comparison of the vacuum tube instrument with a Lindemann quadrant electrometer. In an effort to produce a glass electrode with predictable characteristics there are also reported measurements made on five different soft glass stocks in a buffer series standardized by the hydrogen electrode. Particular interest has been centered in the slope of the line relating potential and PH, the magnitude of the asymmetry potential,[3] and electrical resistance.

Modification of the Vacuum Tube Apparatus.—The circuit for the vacuum tube potentiometer as shown in Fig. 1 has been slightly modified. The high sensitivity galvanometer in the grid circuit is, of course, quite unnecessary for ordinary work. It was inserted only for the purpose of measuring grid leakage while testing various tubes and the effect of varying grid bias potential. Higher sensitivity can be obtained without the shunt around the plate circuit galvanometer, using the latter as a microammeter null instrument, but this arrangement restricts the choice of plate potential, which is determined by the type of galvanometer used and by the construction of the vacuum tube. With the Leeds and Northrup Type P galvanometer (Cat. No. 2239-b, 1000 meg. sensitivity) and Type CX299 tube, a plate potential of 22.5 volts was employed in most of the measurements reported below. The critical grid potential

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[1] Elder and Wright, Proc. *Nat.* Acad. Sci., 14, 936 (1928).

[2] The wiring diagram is shown in Fig. 1. The plate potential of 19.5 volts was supplied from 13 dry cells. Operating on a negative grid bias of 2.3 volts, the UX 222 tube drew less than 10^{-9} ampere in the grid circuit and showed a sensitivity of ±1 millivolt with a Leeds and Northrup wall type galvanometer (sensitivity 10^{-8} ampere) and variable shunt in the plate circuit. The method of measurement was a modification of that proposed by Morton [Trans. Faraday *Soc.*, 24, 14 (1928)] in which an ordinary ("student type") potentiometer was connected in opposition to the cell being measured in the grid circuit. With the paraffin block switch S (Fig. 1) in position "a," the galvanometer was set for *a* certain "zero reading." Then the cell was cut in by throwing S to position "b" and the potentiometer setting changed to bring the galvanometer back to its "zero" position. Thus nearly constant current flow was maintained in the plate circuit and difficulties due to fluctuation in plate potential were minimized. The unknown potential is, of course, the difference between the "zero" and second settings of the potentiometer, which has been independently calibrated against a standard cell in the usual manner.

[3] W. S. Hughes, J. *Chem. Soc.,* 491 (1928).

as estimated by Goode's method[4] for a plate potential of 22.5 volts and filament potential of 2.4 volts for this type of tube is −1.5 volts with reference to the negative filament lead. Any grid bias of greater negative value will be satisfactory in eliminating grid leakage, except that a very large negative grid potential will bring the plate current down to a point where it is less sensitive to change in grid potential. −2.3 Volts is still a satisfactory value for the grid bias of this tube.

The "direct reading hydrogen ion meter" described by Pope and Gowlett[5] offers certain advantages over Goode's apparatus in that the high voltage "B" battery is eliminated and the plate circuit millivoltmeter can be calibrated readily in terms of PH readings before and after each measurement. Both of these circuits, depending on calibration of the indicating instrument in the plate circuit, seem to be fundamentally less reliable than those of the type suggested independently by Morton[2] and Partridge[6] in which the unknown e.m.f. is measured by compensation with a calibrated potentiometer in the grid circuit.[7] The author prefers the single tube outfit since it involves less "B" battery equipment, and with the improvement in sensitivity mentioned above it is possible to measure to ±0.5 millivolt (0.008 PH unit). This sensitivity is more than adequate for work with the glass electrode.

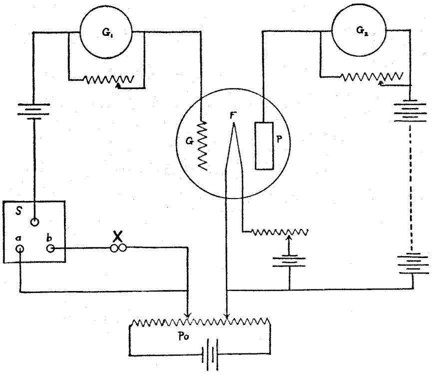

Fig. 1.—G, grid; F, filament; P, plate; G_1, high-sensitivity galvanometer; G_2, wall galvanometer; P_0, potentiometer; S, paraffin block, mercury cup switch; X, glass electrode—Ag, AgCl cell.

Filament temperature is probably the most important variable. Although Goode recommends the oxide-coated filament on account of its longer life, the author found that the thoriated filaments (222 and 199 types) gave approximately 1000 hours of satisfactory service, with only 0.1 ampere from the "A" battery as compared with 0.85 ampere used in Goode's 101-D and 102-D tubes. The lower current consumption is consistent with more constant filament temperature when the ordinary 60 or 100 ampere-hour storage battery is used.

[4] K. H. Goode, J. Opt. *Soc. Am.,* 17, 65 (1928).

[5] Pope and Gowlett, J. *Sci. Inst.,* 4, 380 (1927).

[6] H. M. Partridge, This journal, 51, 1 (1929).

[7] Since this paper was submitted for publication, a description of a "balanced Wheatstone bridge circuit" which also employs the compensation principle, but makes possible the use of a high sensitivity galvanometer as null instrument, has been published by W. C. Stadie [J. *Biol. Chem.,* **83,** 477 (1929)].

When the vacuum tube and its socket are placed in a small tubulated desiccator provided with a drying agent and the leads brought out through a paraffin block in the tubulature, no difficulties are experienced from atmospheric conditions.

Comparison with the Lindemann Electrometer.—The glass cell and potentiometer were connected in series between the electrometer needle and ground, the potential readings being found from the potentiometer setting, with the electrometer functioning as a null instrument.

The electrometer readings were consistently lower than those recorded by the vacuum tube apparatus. The differences *(AE')* varied roughly between 2 and 100 millivolts, the larger differences being consistently associated with high resistances for the glass cells. Table I shows the magnitude of *AE'* for electrodes made from two different soft glasses, measured in a series of buffers. It is obvious that $\Delta E'$ is reasonably constant over the PH range from zero to ten, and about five times as large for the high-resistance electrodes as for those of low resistance.

TABLE I

POTENTIALS OF THE CELL

$\begin{matrix}\mathrm{Hg}\\ \mathrm{Hg_2Cl_2}\end{matrix} \Big| \begin{matrix}\text{Satd.}\\ \mathrm{KCl}\end{matrix} \Big\| \text{Buffer} \Big| \text{Glass} \Big| \begin{matrix}1.0\ N\\ \mathrm{HCl}\end{matrix} \Big| \begin{matrix}\mathrm{Hg}\\ \mathrm{Hg_2Cl_2}\end{matrix}$

Buffer	Electrode E5 Resistance 32 6 megs.			Electrode E8 Resistance 40 2 megs.		
PH	V. T.	Elect.	$\Delta E'$(mv)	V. T.	Elect.	AE' (mv)
0.02	$0.0405	+0.0340	6.5	+0.0380	+0.0350	3.0
1.96	− .0760	− .0810	5.0	− .0745	− .0790	4.5
3.89	− .1960	− .2000	4.0	− .1955	− .2000	4.5
6.02	− .3160	− .3260	10.0	− .3140	− .3210	7.0
7.92	− .4380	− .4430	5.0	− .4430	− .4500	7.0
9.95	− .5580	− .5615	3 5	− .5515	− .5545	3 0
		Average	5.7		**Average**	4.8

Buffer	Electrode WI Resistance 1520 megs.			Electrode W4 Resistance 1010 megs.		
PH	V. T.	Elect.	$\Delta E'$ (mv)	V. T	Elect.	$\Delta E'$ (mv.)
0.02	+0.0465	+0.0200	26.5	+0.0470	$0.0195	27.5
1.96	− .0400	− .0665	26.5	− .0540	− .0700	16.0
3.89	− .1620	− .1860	24.0	− .1720	− .2000	28 0
6.02	− .2720	− ,3000	28.0	− .2820	− .3060	24.0
7.92	− .3590	− .3880	29.0	− .3665	− .3925	26.0
9.95	− ,5175	− ,5475	30.0	− .5350	− ,5525	17.5
		Average	27.3		**Average**	23.7

TABLE II

DIFFERENCES IN VACUUM TUBE AND ELECTROMETER READINGS COMPARED WITH RESISTANCES OF ELECTRODES FROM GLASS STOCK E

Electrode	E2	E4	E5	E6	E8	E11	E12	E13	
AE', mv.	10.5	23.0	6.5	2 5 0	3 0	3 5	2 0 5	2 9 0	
R, megohms	139	139	32 6	190	40 2	26.0	177	326	
$\Delta E'/R$	0.075	0.165	0.199	0.131	0.074	0.135	0.116	0.089	Av. 0.123

TABLE III

DIFFERENCES IN VACUUM TUBE AND ELECTROMETER READINGS COMPARED WITH RESISTANCES OF ELECTRODES FROM VARIOUS GLASS STOCKS

Glass stock	E	CG	W	K	G1
No. of electrodes	8	12	4	5	3
Average $\Delta E'/R$	0.123	0.062	0.026	0.077	0.121
Av. R, megohms	134	256	1270	1450	40

In Table II are listed values of $\Delta E'$ for electrodes all blown from the same glass, but varying widely in resistance. The constancy of the ratio $\Delta E'/R$ as shown in the last line of this table leaves little room for doubt that the difference in apparent potential of the same glass electrode as measured by the two instruments is directly connected with the resistance of the cell as a whole. The value of this ratio, while constant for electrodes prepared from any one glass stock, varies considerably among the five varieties of glass used, as shown in Table III.[8]

The general conclusion to be drawn from the above data is that when a high-resistance cell is connected in series with the grid of a vacuum tube, the latter tends to acquire a free grid potential approximating the critical grid potential which is always more positive than the bias potential. On open circuit the difference is equal to that between the bias potential and critical grid potential, or 800 millivolts. One electrode which showed a resistance of more than 5000 megs. gave a difference of potential on the two instruments amounting to 112 millivolts. The constancy of this difference for any one electrode, however, is responsible for the fact that no error is introduced when P_H values are measured on the vacuum tube apparatus, provided that the glass electrode is checked against at least one standard buffer. Table IV shows the slope $\Delta E/\Delta P_H$ calculated from the data of Table I over the P_H range from 0.02 to 7.92. Within the limits of error indicated (average deviation of the mean of four values) the slope for Sample E agrees with the theoretical, while Sample W shows

TABLE IV

VALUES OF $\Delta E/\Delta P_H$

Electrode	$\Delta E/\Delta P_H$ on vacuum tube	$\Delta E/\Delta P_H$ on electrometer	$\Delta E/\Delta P_H$ theoretical for 25°
E5	0.0607 ± 0.0013	0.0604 ± 0.0006	0.0591
E8	.0610 ± .0021	.0615 ± .0019	.0591
W1	.0513 ± .0030	.0516 ± .0030	.0591
W4	.0523 ± .0022	.0521 ± .0038	.0591
CG	.0584 ± .0026	....	.0591
G1	.0603 ± .0021	..	.0591
K	.0589 ± .0022		.0591

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[8] Stadie has also pointed out that the free grid potential, $\Delta E'$ (see next paragraph) varies not only with the external grid resistance, but also with those factors which influence plate current, notably filament temperature.

a low value, in agreement with Hughes' results on the same glass. Average slopes for the other three glasses are also included in the table.

Resistance Measurement.—A Leeds and Northrup Type R galvanometer (Cat. No. 2500-b 2000 megohm sensitivity) was roughly calibrated by a 10-megohm grid leak, showing a sensitivity of 2040 megohms. Using these calibration data and the same source of potential (1.5 volts), the resistances of the various glass cells were calculated directly from the observed deflections, making corrections for the resistance of the electrolyte from blank measurements. The lower resistances can be taken as reliable to ±1 megohm, but the higher values are proportionately uncertain and this fact may be responsible for the variations in $\Delta E'/R$ shown in Table III.[8]

Glass Stocks.—The symbols used in this paper indicate the following soft glasses: E, a special glass made in this Laboratory as described in the preceding paper (ref. 1, p. 938); CG, Corning soft glass G8, Corning Glass Co., Corning, N. Y.; W, Wood Bros. "white flint," Wood Bros. Glass Co.,[3] Barnsley, Yorkshire, England; K, Kimball machine drawn tubing, Kimball Glass Co., Vineland, N. J.; Gl, unidentified.[9]

Asymmetry Potential.—As pointed out in the preceding paper,[1] an electrode for PH measurement must be reversible and readily reproducible, or else it must be frequently checked against one or more standard buffers. The latter procedure is recommended by Kerridge for the glass electrode.[10] In the hope of finding conditions under which a glass electrode could be made reproducible, the effects of strenuous polarization and of annealing on the asymmetry potential have been studied. The latter has been described by Hughes.[3] Its value is given by the difference between the potentials of the following two cells.

$$\text{Cell 1.}\quad \begin{array}{c|c||c|c|c|c} \text{Hg} & \text{Satd.} & 1.0\ \text{N} & & 1.0\ N & \text{Hg} \\ \text{Hg}_2\text{Cl}_2 & \text{KCl} & \text{HCl} & \text{Glass} & \text{HCl} & \text{Hg}_2\text{Cl}_2 \end{array}$$

$$\text{Cell 2.}\quad \begin{array}{c|c||c|c} \text{Hg} & \text{Satd.} & 1.0\ \text{N} & \text{Hg} \\ \text{Hg}_2\text{Cl}_2 & \text{KCl} & \text{HCl} & \text{Hg}_2\text{Cl}_2 \end{array}$$

Repeated measurements of Cell 2, after one or two hours' standing to allow diffusion to set up a constant junction potential, show a value of the e.m.f. of 0.0315 volt.[11]

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[9] This glass, taken from our laboratory soft glass stock, was traced to Glasco Products, Chicago, Ill., who described it as their "special cut glass." A sample which was kindly sent to the author by the above firm as a first approximation to the original shows the following properties: asymmetry potential, +0.0125; $\Delta E'/R$, 0.178; slope, 0.0510; average resistance high, about 300 to 400 megohms for electrode.; of the bulb type. Further efforts are being made to duplicate the original sample.

[10] Kerridge, *Biochem.* J., 19, 611 (1925).

[11] From the data of Scatchard [THIS JOURNAL, 47, 696 (1925)] on the cell, Hg, Hg_2Cl_2 | Satd. KCl || HCl, 1.0008 M | AgCl, Ag with flowing junction, and from the data of Gerke [*ibid.*, 44, 1684 (1922)] on the cell Ag, AgCl | Cl^- | Hg_2Cl_2, Hg, the value of the e.m.f. of Cell 2 is calculated to be 0.0295. The difference of 2 millivolts is probably due to the fact that Scatchard's measurements refer to a cell with flowing junction, whereas the cell measured by the author had a diffusion junction.

TABLE V

ASYMMETRY POTENTIALS

Electrode glass	Controls untreated	Treated Electrodes Polarized neg.	Polarized pos	Annealed	Prepd. by method of MacInnes and Dole
E	+0.0049 ± 0.0011	+0.0098	+0.0030	+0.0035	......
CG	− .0413 ± .0040	+ .0035	− .0410	− .1055	+0 0010
W	− .0144 ± .0033	......	......	......	......
G1	− .0103 ± .0024	......	......	− .0615	......
K	− .0640 ± .0062	......	......	− .1550	+ .0045

On account of the free grid potential effect which is observed in using the vacuum tube apparatus, all the above measurements (Table V) were made on the Lindemann electrometer.

Treatment of Electrodes

Polarization.—To test the reversibility of the phase boundary equilibrium at a glass surface, a number of the electrodes listed in Table V were connected across a source of 110 volts d. c. by means of platinum wires and left in the circuit for fifteen to twenty hours. The electrolyte used was 1 N hydrochloric acid, inside and out. As shown in the table, the electrodes whose inside connection was positive (anodic polarization) came back after about three days to a value which agrees with the average for the control electrodes within the limits of variability of the latter. Measurements repeated after nine days on the same electrodes showed no further variation beyond these limits. Those electrodes whose inside connection was negative (cathodic polarization) showed an appreciably higher potential after three days, the potential again being constant for the six days subsequent. Thus it appears that the passage of hydrogen ion into the outer surface of glass is the less reversible process.

Annealing.—On the assumption that the asymmetry potential may be due, at least partly, to a difference in total surface energy between the inner and outer surfaces of the glass bulb, it was thought that a mild annealing process, tending to reduce mechanical strains, might also affect the asymmetry potential. The electrodes in question were put in an oven immediately after they were blown (with one exception, *viz.*, CG83) and heated to 120° for fifteen to twenty hours. The surprising results are shown in Table V.

With one exception (E8) all the electrodes which were annealed showed potentials from 50 to 100 millivolts low as compared to the average of the controls. The potentials listed in the table for Glass CG were read nine days after annealing and are about thirty millivolts more positive than they were one day after annealing. Thus there is a slow continuous drift back to the normal value as represented by the control electrodes. From these experiments it appears that whatever effect annealing may have on reducing mechanical strain is overshadowed by some other effect, the nature of which is still obscure.

Method of Preparation.—Unless otherwise indicated all the electrodes were prepared as thin-walled bulbs blown from 10 to 14-mm. tubing. MacInnes and Dole have described an alternative method for preparing very thin glass membranes which seems to offer decided advantages.[12] Electrodes were prepared by this method from the two glass stocks which showed the highest asymmetry potentials among the untreated electrodes (CG and K). In each case the electrodes so prepared had asymmetry poten-

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[12] MacInnes and Dole, Ind. *Eng. Chem. Analytical Edition*, **1,** 57 (1929).

tials no greater than the probable uncertainty of the controls. It is interesting to note that one of these, K4, has a resistance of the order of 5000 megohms, while CG813 measures only 5.7 megohms.

P_H Measurement by the Glass Electrode without the Use of Standard Buffers.—Since the asymmetry potential seems to be specific for any one stock of glass and independent of age or resistance, it is suggested that the above data might be employed in measuring an unknown P_H with an electrode prepared from one of the glasses listed.

For example, the P_H of a solution in which an electrode prepared from the Corning glass and filled with 1.0 N hydrochloric acid shows a potential against saturated calomel of the value "E" is given as

$$P_H = 0.085 - \frac{E - (-0.0413 + 0.0315)}{0.0581}$$

Summary

The vacuum tube potentiometer as described by Elder and Wright has been modified with a view to increasing the sensitivity and simplicity of the apparatus.

Comparative measurements on the vacuum tube potentiometer and Lindemann electrometer show that the apparent potentials of high resistance glass cells measured on the former instrument include a free grid potential which is constant over the P_H range from zero to ten, and directly proportional to the glass cell resistance.

Four commercial stock soft glasses and one laboratory preparation were studied in a series of buffers which had been standardized by the hydrogen electrode.

The asymmetry potentials of electrodes of the bulb type measured in 1 N hydrochloric acid are constant for any one glass stock and vary from 5 millivolts ior the laboratory preparation to 64 millivolts for one of the commercial stocks.

The effect of anodic polarization by 110-volt d. c. for fifteen to twenty hours disappeared completely after three days. Cathodic polarization by the same applied voltage for the same time produced a polarization potential of 40 to 50 millivolts after three days which persisted for six days more.

Annealing for fifteen to twenty hours at 120° caused a decrease in potential which was variable and very slow in disappearing.

The asymmetry potentials of electrodes prepared by the method of MacInnes and Dole were uniformly low, irrespective of the glass used.

Methods are suggested whereby the data presented in this paper could be used for P_H measurement by the glass electrode without employing standard buffers.

URBANA, ILLINOIS

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

THE USE OF DICHLOROFLUORESCEIN AS AN ADSORPTION INDICATOR FOR THE ARGENTOMETRIC TITRATION OF CHLORIDES

BY I. M. KOLTHOFF, W. M. LAUER AND C. J. SUNDE

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Introduction

K. Fajans and his collaborators[1] have recently described a new type of indicator for the argentometric titration of halides to which the name of adsorption indicator was given. The substances used as indicators are not sensitive to dissolved silver or halide ions, but change their color at the equivalence point where colored compounds are formed on the precipitate due to adsorption phenomena. Other investigators[2] have confirmed the results of Fajans and his collaborators and obtained accurate results with the new type of indicator. Fluorescein has been used as the indicator in the titration of chlorides but its application is limited. Good results are obtained only if the chloride concentration is greater than 0.005 N and if the solution has a neutral or weakly alkaline reaction. Other indicators which were applicable in weakly acid solutions have been found, but the color changes are less distinct than is the case with fluorescein.[3]

When chloride ions are titrated with silver nitrate, the silver chloride adsorbs silver ions at the equivalence point or better slightly beyond. The "silver body" then adsorbs fluorescein ions from the solution and dark red silver fluoresceinate is formed on the surface of the precipitate. Fluorescein possesses a weak acidic character; in weak acid solution the concentration of fluorescein ions is so small that the color change no longer takes place. The introduction of halogen atoms into the fluorescein molecule has two effects: the dissociation constant is increased and the adsorbability of the dye anions by the silver halide increases. It would therefore be expected that substances with a stronger acid character than fluorescein could be used as indicators in weak acid solutions. On the other hand, the stronger adsorbability might either interfere or be favorable. During the titration of chloride ions with silver nitrate the silver chloride formed at the beginning of the titration adsorbs chloride ions. In the presence of the anions of the indicator, the latter also have a tendency to be adsorbed and if their adsorption is larger than that of the chloride ions, the color change will take place during the early stages of the titra-

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[1] (a) Fajans and Hassel, Z. *Elektrochem.*, 29, 495 (1923); (b) Fajans and Wolff, Z. anorg. *allgem.* Chem., 137, 221 (1924).

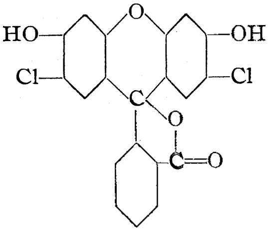
[2] W. Bottger and K. O. Schmidt, *ibid.*, 137, 246 (1924); I. M. Kolthoff and L. H. van Berk, *Z.* anal. *Chem.*, 70, 369 (1927).

[3] Kolthoff, *ibid.*, 71, 235 (1927).

tion. Such is the case when eosin is used. Therefore this indicator cannot be used in the argentometric determination of chlorides, even though it gives highly accurate results when bromides, iodides and thiocyanates are titrated even in weak acid solutions. On the other hand, stronger adsorbability may exert a favorable influence in that it might make possible the titration of very dilute chloride solutions. In this case, the absorption of fluorescein ions is too small and no color change is observed.

The indicator in order to be better than fluorescein must have a larger dissociation constant and greater adsorbability than fluorescein. The adsorbability, however, must not be so great that it replaces the chloride ions from silver chloride. It was expected that dichlorofluorescein would serve the purpose, and as is shown in the following part of this paper it proved to be an excellent indicator for the titration of chlorides under different conditions. That dichlorofluorescein is a stronger acid than fluorescein can easily be shown by the fact that its color change interval from green-yellow (without fluorescence) to a strongly fluorescent yellow-green lies between P_H 3 to 5; so that the dissociation constant is of the order of 10^{-4}.

Dichlorofluorescein.—Dichlorofluorescein was prepared by condensing monochlororesorcinol with phthalic anhydride. It was purified by converting it into the diacetate and then saponifying the diacetate with alcoholic potassium hydroxide, in accordance with the procedure used by Orndorff and his collaborators.[4] Dichlorofluorescein prepared from dichlorophthalic anhydride and resorcinol has been known for some time, but dichlorofluorescein containing two chlorine atoms in the "resorcinol part" of the molecule has not been described hitherto. The most probable formula for the dichlorofluorescein here described is that indicated. All attempts to prepare a dichlorofluorescein by the direct chlorination of fluorescein failed.



Experimental

The Preparation of Dichlorofluorescein

Monochlororesorcinol was first prepared by the action of sulfuryl chloride on resorcinol: 100 g. of resorcinol was dissolved in 360 g. of absolute ether. This solution, placed in a 2-liter round-bottomed flask fitted with an efficient reflux condenser, was then treated with 120 g. of sulfuryl chloride (added dropwise). This operation was carried out in a well-ventilated hood. After the addition of the sulfuryl chloride the ether was distilled off on a steam-bath. After the low-boiling material had been removed completely, the residue was subjected to vacuum distillation. Since monochlororesorcinol has a lower boiling point than resorcinol, the unchanged resorcinol was separated by vacuum frac-

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[4] Orndorff and Hemmer, THIS JOURNAL, 49, 1275 (1927), and various other studies by Orndorff and co-workers.

tional distillation. The monochlororesorcinol distilled at 131° under a pressure of 6–7 mm. It was analyzed for chlorine by the method of Carius.

Anal. Calcd.: Cl, 24.54. Found: Cl, 24.50, 24.72.

Dichlorofluorescein.—Ten grams of phthalic anhydride mixed intimately with 19.7 g. of monochlororesorcinol was heated to 160° in an iron crucible by means of an oil-bath. Five grams of anhydrous zinc chloride, finely ground, was then added with stirring during a period of about ten minutes. The temperature was then raised to 175–180° and maintained for about two and one-half hours. After cooling, the reaction product was ground and then boiled for fifteen to twenty minutes in dilute hydrochloric acid (10 cc. of concd. acid to 200 cc. of water) and filtered.

The precipitate was dissolved at room temperature in a saturated aqueous solution of sodium bicarbonate, filtered, heated to boiling and then acidified with hydrochloric acid (approx. 4 N). After cooling and filtering, the precipitate was refluxed with acetic anhydride for several hours (2 g. of crude dichlorofluorescein to 10–12 cc. of acetic anhydride). The diacetate crystallized out upon cooling. It was filtered off and the above process repeated four or five times. The diicetate (almost colorless) was then digested with a small amount of alcohol, cooled and filtered. After drying for several hours at 100° it was analyzed for chlorine.

Anal. (Carius). Calcd.: Cl, 14.64. Found: Cl, 14.49, 14.98.

The diacetate was then saponified by refluxing 2–3 g. with alcoholic potassium hydroxide (6–7 *g.* of base in 40 cc. of alcohol) for two hours. Water was then added, the solution transferred to a distilling flask and the alcohol removed by distillation. The solution was then filtered (if necessary), heated to boiling and acidified with hydrochloric acid. An ochre-colored product was obtained.

Application to Halide Titrations

Indicator Solution.—One-tenth gram of the indicator was dissolved in 60 cc. of alcohol, 2.5 cc. of 0.1 *N* sodium hydroxide was added and the volume of the solution was then made up to 100 cc. with distilled water. An aqueous alcoholic solution (60–70%) of approximately the same concentration of unneutralized indicator may also be used.

Procedure.—For every 10 cc. of chloride solution 2 drops of indicator are added and the titration is started with silver nitrate. The silver chloride remains in colloidal solution which, near the end-point, has a yellowish-orange appearance. About 0.5% before the equivalence point the silver chloride flocculates in voluminous flocks; the titration is then conducted carefully. At the end-point the silver chloride suddenly turns dark red.

Note 1.—Concentrated chloride solutions should be diluted to a salt-concentration of about 0.025 N. In this case the color change is extremely sharp. In six titrations 100 cc. of 0.025 *N* sodium chloride required 25.00 to 25.03 cc. of 0.1 *N* silver nitrate.

Note 2.—Even very dilute chloride solutions can be determined satisfactorily. In these cases it is recommended not to add more than 2 to 4 drops of indicator to 50 cc. of solution.

A 0.01 *N* chloride solution can be titrated with an accuracy of 0.5%. Near the end-point the liquid appears more brownish; the titration is finished when the color changes to distinct orange. One or two drops of 0.01 *N* silver nitrate in excess deepens the color to pink or reddish.

If the end-point is passed the excess of silver nitrate can be titrated back with a chloride solution of known constant. This reverse titration should be made immediately after the addition of silver nitrate. After longer standing the adsorbed indicator reacts slowly.

The following data show that the method gives satisfactory results.

TABLE I

TITRATION OF DILUTE CHLORIDE SOLUTIONS

Sodium chloride, cc.	10 of 0.01 *N*	50 of 0.002 *N*	100 of 0.001 *N*
0.01 *N* $AgNO_3$, cc.	10.02 to 10.05[a]	10.05 to 10.15	10.10 to 10.15[b]
0.01 *N* $AgNO_3$ calcd., cc.	10.00	10.00	10.00

[a] End-point of an orange color which turned pink after addition of 10.07 to 10.09 cc. of 0.01 *N* silver nitrate solution.

[b] With a larger excess of silver nitrate the color became more intense.

Especially in these very dilute solutions the back titration with chloride gives a sharp end-point.

Solutions containing as little as 15 to 20 mg. of chloride in a liter can be titrated with an accuracy of 1 to 2%. Therefore the method is superior to the ordinary Mohr procedure, as the latter has an appreciable titration error (at those dilutions). It might be expected that the indicator can be used advantageously in the titration of chloride in tap water. Special tests were run in order to see if calcium bicarbonate, magnesium bicarbonate and other salts had an interfering action. Though larger amounts of salts, especially those containing higher valence cations affect the color change a little, the results were still accurate to about 2% in 0.002 N chloride solution.

The tap water of Minneapolis contains only 2.6 mg. of chloride in a liter, which is too small to be titrated. Moreover, it seems that the tap water of this city contains some interfering substance. If a 0.001 N chloride solution prepared in tap water was titrated, no color change at all was observed. With artificial water of the same chemical composition as the tap water of Minneapolis and containing 1 milliequivalent of chloride in a liter a good end-point was observed. Even in the titration of 0.01 *N* chloride solution the tap water had a distinct retarding action on the formation of the color change. In all these cases it was observed that in the presence of tap water the silver chloride did not flocculate at all or very slowly with an excess of silver nitrate. Therefore it was thought that protecting colloids in the tap water might interfere with the observation of the end-point. The influence of different hydrophyllic colloids was tested. Some of them, especially gelatin even in small concentration, make the color change much less distinct and the end-point appears late. The presence of traces of colloidal material may explain the peculiar behavior of the Minneapolis tap water. On the other hand, it was shown that a dilute solution of silicon dioxide (from sodium silicate and acid) did not affect the color change of the indicator.

Another advantage of the new indicator over potassium chromate is that the titration can be carried out in weakly acid solution. If the acidity is regulated by some buffer in such a way that the PH is larger than about

4.0, the color change is still very distinct. In the titration of 0.025 N sodium chloride solution in the presence of an acetate buffer with a PH equal to or greater than about 4.4, the first color change to orange occurred after overstepping the end-point 0.1 to 0.2%. An advantageous application of the method is a direct chloride titration of those salts of heavy metals which are slightly hydrolyzed. Mohr's method gives unsatisfactory results in the above cases. In the titration of 0.025 N (to chloride) solutions of copper, zinc, manganese, nickel, aluminum, calcium, strontium, barium and magnesium chloride, the end-point was very sharp and appeared at the right place. In most cases the silver chloride flocculated 50 to 20% before the end-point was reached. Near the equivalence point the precipitate was slightly colored. At the equivalence point the sudden increase of the color to intense red could be observed with an accuracy of 0.05 cc. of 0.1 N silver nitrate. In the titration of very dilute solutions it is better to work at neutral reaction.

Bromides and iodides can be titrated in the same way as chlorides, even in very dilute solutions. In the application of fluorescein as an indicator, K. Fajans and H. Wolff[1] found that a mixture of iodide and chloride required an excess of silver nitrate, the error being +1 to 1.5%. Therefore, the use of the dichlorofluorescein for this purpose was tested. During the titration the same phenomena are observed that Fajans and Wolff described; about 2% before the end-point the silver iodide and chloride flocculate, the precipitate has a yellowish-brown color which turns brown-orange at the equivalence point and changes to orange-pink with an excess of about 0.5% silver nitrate. Though the color change is not as sharp as in the titration of both halides separately, the end-point still can be detected with an accuracy of 0.5%, if the mixture is so far diluted that its concentration is no more than 0.01 N to halide. The change in color in this case is much sharper than with fluorescein as an indicator.

Summary

Dichlorofluorescein is a very suitable indicator for the argentometric titration of chlorides in very dilute as well as in weakly acid solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

THE PERMEABILITY OF HOT METALS TO HYDROGEN[1]

BY B. CLIFFORD HENDRICKS AND ROBERT R. RALSTON

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A paper[2] which appeared in December, 1923, reported a preliminary study of the diffusion of hydrogen through hot metals. In July of that year Lombard[3] published the results of a study of the diffusion of hydrogen through nickel and the following year Johnson and Larose[4] presented their work upon the diffusion of oxygen through silver. A second paper from Johnson and Larose[5] gives both improved apparatus and a changed interpretation. Lombard has published two papers[6] upon diffusion since his first. The first of these makes a comprehensive analytical study of the available data upon hydrogen diffusion through nickel. The second deals with experiments with other gases including argon, nitrogen and helium, and with other metals such as copper, iron and platinum. In his last paper he also attempts to formulate a generalization for all such diffusion.

It is proposed in this paper to give a restudy of copper and zinc as diffusion diaphragms for hydrogen and to measure diffusions through nickel under varying temperatures and pressures of the gas. The results obtained, as well as those of other students of diffusion, are to be studied for the relation of diffusion values to the different conditioning factors.

This work, while using essentially the same apparatus as that already described,[2] has introduced certain modifications of that practice. By introducing Swartz tubes filled with phosphorus pentoxide, in addition to soda-lime tubes used in the former research, "blank values" have been reduced from 1.5 mg. per hour to 0.4 mg. per hour or less. By permitting the outlet[2] from the hydrogen chamber to terminate in a pipet dipping beneath the surface of a carefully graduated cylinder of mercury, the hydrogen pressure has been regulated and maintained at the desired value in spite of fluctuations of the atmospheric pressure and changes in other variable influences in the train.

Varying pressures of the diffusing gas, hydrogen, have been secured by mixing hydrogen and nitrogen in varying proportions. The gasometer used was calibrated and read within an accuracy of 0.5%. Lom-

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[1] Read before the Physical and Inorganic Division of the American Chemical Society at Columbus, Ohio, April, 1929.

[2] Deming and Hendricks, THIS JOURNAL, 45, 2857–2864 (1923).

[3] Lombard, *Compt. rend.*, 177, 116 (1923).

[4] Johnson and Larose, THIS JOURNAL, 46, 1377 (1924).

[5] Johnson and Larose, *ibid.*, 49, 312 (1927).

[6] Lombard, *J. chim. phys.*, 25, 501, 587 (1928).

bard[7] found by experiments with similar mixtures that the diffusion rate of the hydrogen was independent of the presence of the nitrogen in the mixtures. He[8] also found that the diffusion rate of hydrogen through nickel varied inversely with the thickness of the metal. Thus Fick's law correctly describes the diffusion of hydrogen through nickel. By the aid of Fick's law the specific diffusion of hydrogen through hot metals is here expressed as the number of milligrams of hydrogen diffusing per square meter of surface per millimeter thickness of metal per hour. In arriving at this specific diffusion for different temperatures, corrections were made, in every instance, for the increase of both the diaphragm area and thickness due to thermal expansion. This increase varied both with the kind of metal used and with the temperature change.

The temperatures were measured by a chromel–alumel thermocouple calibrated for the melting points of Mallinckrodt C. P. tin and zinc and General Chemical Company aluminum. The millivoltmeter for the thermocouple was read to 0.1 millivolt, which corresponded to less than 3°. The cold junction of the couple was kept in an ice pack in a Dewar container.

The gases used were secured and purified as described in the previous paper except for the before-mentioned drying.

The diffused hydrogen, as in the former work, was oxidized to water by hot copper oxide and collected by absorption in phosphorus pentoxide-filled U-tubes. These were always weighed counterbalanced by a U-tube of equal volume kept in the balance case. The tube to be weighed was always cooled and filled with dry air before weighing.

Zinc.—The sample of zinc[9] used in this study contained not more than 0.1% of lead, 0.005% of cadmium and 0.008% of iron, Its purity was the same as that of the sample used in the work[2] previously reported. The disk used had a thickness of 0.515 mm., while 1.643 mm. was the thickness of the sample tested in the earlier work. Its diffusion area at the temperatures of the experimental work was 1.7% greater than at room temperature. Table I exhibits the summarized results of over twenty hours of work with this metal. The temperature deviation from the

TABLE I

RESULTS WITH ZINC

Thickness, 0.515 mm.; area, 47.78 sq. cm. at 20°; average "blank" for three runs, 0.3 mg. per hour; hydrogen partial pressure, 1.000 ± 0.007 atm.

Mean temperature, °C.	305	373
Water collected, mg. per hour	0.9±0.2	3.0±0.4
Sp. diff. of hydrogen through zinc	8.0±4.0	32.2±4.8

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[7] Lombard, J. *chim. phys.*, *25*, 519 (1928).

[8] Lombard, *ibid.*, 25,527 (1928).

[9] Generously supplied by the New Jersey Zinc Company.

mean value was in all cases, in this and in the following tables, less than the precision of the thermocouple.

These values leave no doubt that zinc is hydrogen permeable and that it becomes increasingly so with higher temperatures. A study of the plate before and after the diffusion experiments showed a decrease in crystal size as a result of its exposure to hydrogen at these temperatures near its melting point.

Copper.—Sieverts,[10] after a series of tests, concluded that pure copper was permeable to hydrogen above 640° with no effect upon the copper. However, he found that commercial copper tubes changed, "became brittle and fissured," in an atmosphere of hydrogen. A similar result was reported by Deming and Hendricks in a previous paper.[2] Lombard[11] states that a trial with copper resulted in "a rapid and progressive increase in the diffusion value even when the temperature and pressure were held constant."

The copper used in the present work had been carefully deoxidized by phosphorus.[12] It was 99.900% pure before this phosphorus reduction. Even though pure and oxygen-free, some difficulty was experienced in getting the limited data presented in Table II.

TABLE II

RESULTS WITH COPPER

Thickness, 0.385 mm.; area, 46.56 sq. cm. at 20°; average "blank" for two runs, 0.2 mg. per hour; hydrogen pressure, 1.000 ± 0.007 atm.

Mean temperature, °C.	497	568	632
Water collected, mg. per hour	2.2 ± 0.3	3.35 ± 0.5	6.5 ± 0.7
Sp. diff. of hydrogen through copper	17.3 ± 1.8	28.9 ± 0.4	57.7 ± 6.5

Microscopic examination of this sample, after the diffusion tests, showed a decided increase in crystal size. A similar change was reported in the previous paper[2] though the intercrystalline cracks were there attributed to the reducing action of hydrogen upon inclusions of cuprous oxide. The previous treatment of the copper samples, here used, would make that explanation untenable. A more plausible hypothesis might well be that increased crystal size gives rise to larger crystalline planes of cleavage. These planes, as they more and more nearly extend through the thin plate, presently become mechanical openings or fissures, rendering the copper more permeable as well as more brittle.

The above results, it should be noted, do not agree with Sievert's either in regard to the lowest temperature at which diffusion through copper takes place or in the effect of diffusion upon the pure copper metal.

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[10] Sieverts, *Z. physik. Chem.*, *60*, 188–201 (1907).

[11] Lombard, *J. chim. phys.*, 25,590 (1928).

[12] These samples were generously prepared and furnished by the American Brass Company.

Nickel.—The nickel used[13] was electrolytically refined. After **100** or more hours of exposure to hydrogen gas at high temperatures, this metal showed no change either in crystal size or in diffusion rate. Such consistency was very advantageous to work which sought both the effect of temperature variations upon diffusion rate and the influence of pressure changes upon that phenomenon. Results for three different pressures of the diffusing hydrogen through nickel are presented in Table III A, B and C.

TABLE III

RESULTS WITH NICKEL

Thickness, 0.423 mm.; diffusion area, 46.56 sq. cm. at 20°; average "blank" for four runs, 0.4 mg. per hour.

Mean temp., °C.	Water coll., mg. per hour	Sp. diff. of hydrogen through nickel
Part A		
Hydrogen pressure, 1.000 ± 0.007 atm.		
478	3.8 ± 0.7	34.21 7.0
503	5.45 ± 0.05	50.6 ± 0.7
553	9.0 ± 1.3	82.3 ± 9.0
570	9.2 ± 1.6	88.6 ± 16.3
640	14.9 ± 0.9	144.7 ± 8.5
678	18.0 ± 0.5	176.71 4.5
703	20.7 ± 1.7	202.4 ± 16.9
747	24.9 ± 2.0	238.6 ± 14.4
798	37.7 ± 0.9	369.2 ± 8.8

Mean temp., °C.	Water coll., mg. per hour	Sp. diff. of hydrogen through nickel
Part B		
Hydrogen partial press., 0.514 ± 0.009 atm.		
471	3.3 ± 0.7	28.7 ± 6.5
532	5.9 ± 0.3	54.8 ± 3.5
597	8.6 ± 1.3	81.7 ± 13.5
619	11.3 ± 0.2	109.4 ± 2.0
665	12.6 ± 1.1	122.4 ± 10.1
677	14.2 ± 1.7	133.4 ± 21.3
Part *C*		
Hydrogen partial press, 0.150 ± 0.01 atm		
498	2.7 ± 0.8	23.1 ± 8.0
577	4.4 ± 0.2	39.7 ± 2.4
658	7.0 ± 0.3	65.4 ± 3.5
719	10.4 ± 1.0	94.2 ± 4.4

Diffusion and Pressure.—In order to study the relation of diffusion rate to pressure at constant temperatures, the data presented in Table III A, B and C above were put in graphic form as in Fig. 2 in the first paper.[2] From these curves the values tabulated in the first horizontal line, for each temperature, in Table IV were obtained.

Richardson, Nicol and Parnell,[14] Lombard[15] and Johnson and Larose[16] have all intrepreted their experimental data for pressure variation by a relationship expressed by $D = K\sqrt{P}$, in which D is the specific diffusion, P is the partial pressure of the diffusing gas and K is a constant varying with the temperature. For this paper this constant was determined for each of the four temperatures by the graphic method. The values found were: 76.2 for 550°, 116.0 for 600°, **152.2** for 650° and **190.0** for 700°. The second horizontal line under each temperature of Table IV records specific diffusion values calculated by use of this constant in

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[13] The samples were generously furnished by the International Nickel Co.

[14] Richardson, Nicol and Parnell, Phil. *Mag.*, [6] 8, 1 (1904).

[15] Lombard, J. *chim. phys.*, 25,518,593 (1928).

[16] Johnson and Larose, THIS JOURNAL, 49,317 (1927).

TABLE IV

RELATION OF SPECIFIC DIFFUSION TO PRESSURE

Temp., °C.			Specific diffusion values in atmospheres for the pressures 1.000	0.514	0.150
550	1	From graphs	80.0	60.0	35.0
	2	Calculated	76.2	54.6	29.5
	3	Observed (553°)	82.3±9.0		
600	1		110.0	85.0	47.5
	2		116.0	83.1	44.9
	3	(597°)		81.7±13.5	
650	1		150.0	115.0	65.0
	2		152.2	109.1	58.9
	3	(658°)			65.4±3.4
700	1		197.5	147.5	85.0
	2		190.0	136.2	73.5
	3	(703°)	202.4±16.9		

the equation above. The third horizontal line in the table exhibits specific diffusion values, with their deviations from the mean, obtained directly by experiment for the temperatures shown in parentheses. The calculated values, it should be noted, show no greater deviation from the observed values than do the observed from their own mean.

Diffusion and Temperature.—Three different expressions have been put forth for the correct relation of diffusion rate to temperature: $D = KT^b$; $D = K \times 10^{at}$ and $D = KT^{1/2}e^{-q/4T}$.

The first was proposed by Ryder[17] and was used by Johnson and Larose[4] in 1924 in connection with their study of the diffusion of oxygen through silver. The expression may be put in the form $\log D = \log K + b \log T$, which lends itself to graphic representation. The authors find that when their data for the diffusion of hydrogen through nickel are so plotted, the result is not a first-order curve. Johnson and Larose in their second paper,[5] for the same reason, decided against this expression for the temperature–diffusion relationship. In other words, this formulation is inadequate either for the diffusion of oxygen through silver or the diffusion of hydrogen through nickel.

The second equation, $D = K \times 10^{at}$, is that which Lombard[18] claims to represent acceptably the relation of diffusion to temperature for his study of hydrogen and nickel as well as for other gases through other metals. His evidence for his conclusion is that when log D is plotted against T, the curve resulting is of the first order. A critical examination of Lombard's curves does not lead the authors to his conclusions. Neither does such graphic treatment of their own data lead to his generalization. In fact they have found that whether Lombard's work with hydrogen and nickel, their own work with hydrogen and nickel, Johnson and

[17] Ryder, *Elect. J.*, 17, 161 (1920).

[18] Lombard, *J. chim. phys.*, 25, 597 (1928).

Larose's work with oxygen and silver or Richardson, Nicol and Parnell's work with hydrogen and platinum, is given this graphic form, the curve is invariably concave toward the temperature axis and convex toward the diffusion axis.

Johnson and Larose in their second paper[5] show that $D = KT^{1/2}e^{-q/4T}$ gives a much more satisfactory generalization for the diffusion of oxygen through silver than did the Ryder formulation, $D = KT^{b}$, which they first used. The expression is a derivation from the more general form: $D = K/dP^{1/2}T^{1/2}e^{-q/4T}$, when P and d are assumed as constants. This general equation was set up from thermodynamic considerations[19] and connects specific diffusion, D, with absolute temperature, T, diaphragm thickness, d, and pressure, P. In it "e" is the base for the natural system of logarithms, q is a constant representing the heat of dissociation of the gas within the metal and K is a general constant. A simple method of applying this relationship to a set of data is to plot the reciprocal of the temperature, $1/T$, against log D − $^1/_2$ log T. The authors show the graph resulting for data from their Table III A in Curve H and in Fig. 1. For comparison purposes they have also included curves for hydrogen through platinum, R, oxygen through silver, J, and hydrogen through

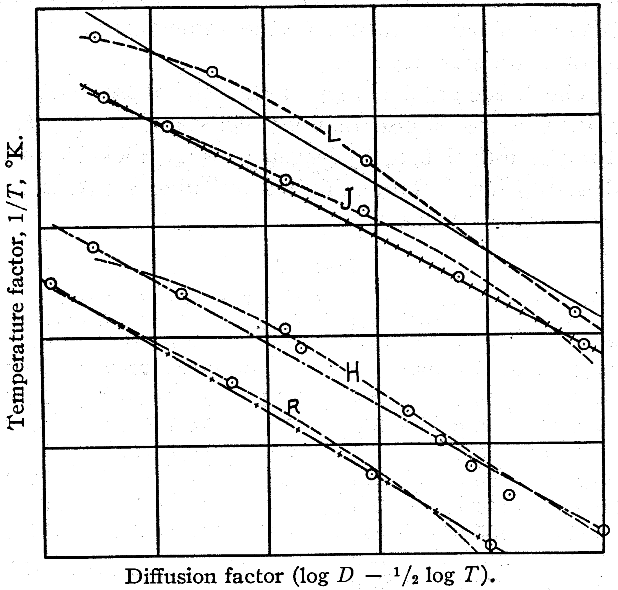

Fig. 1.—Relation of diffusion rate to temperature for: R, Richardson's hydrogen through platinum; J, Johnson's oxygen through silver; H, authors' hydrogen through nickel; L, Lombard's hydrogen through nickel.

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[19] Richardson, *Phil. Mag.*, [6] 7, 266 (1904).

nickel, L, in the same figure.[20] The essential point sought in the figure is to show that, within the limits of experimental error, Richardson's equation represents the temperature–diffusion relationship for the diffusion of hydrogen through platinum and nickel and of oxygen through silver.

The authors cannot refrain, however, from pointing out that the broken-line curves, as drawn in Fig. 1, are not an undue distortion of the points as located. The graph, L, of Lombard's data especially makes evident the concavity of these curves toward the origin. For work so far reported, experimental values probably deviate from their means by amounts sufficient to "iron out" such concavity. Yet why do all four of these curves consistently show curvature in the same direction? Probability can hardly account for such regularity.

In order to check the applicability of the Richardson equation to data under study in a more precise manner, constants q and K have been determined for the diffusion of hydrogen through nickel and the specific diffusions calculated for all data exhibited in Table III A, B and C. The results are presented in Table V.

TABLE V

COMPARISON OF CALCULATED RATES OF DIFFUSION WITH THOSE OBSERVED

Temp., °C.	Diffusion Observed	Diffusion Calcd.	Dev. of calcd. from obs.
Hydrogen pressure, 760 mm.			
478	34.2 ± 7.0	38.1	+3.9
503	50.6 ± 0.7	48.6	−2.0
553	82.3 ± 9.0	75.3	−7.0
570	88.6 ± 16.3	86.3	−2.3
640	144.7 ± 8.5	144.3	−0.4
678	176.7 ± 4.5	185.0	+8.3
703	202.4 ± 16.9	215.6	+13.2
747	238.6 ± 14.4	277.5	+38.9
798	369.2 ± 8.8	362.6	−6.6
Hydrogen pressure, 390.6 mm.			
471	28.7 ± 6.5	25.6	−3.1
532	54.8 ± 3.5	45.2	−9.6
597	81.7 ± 13.5	76.2	−5.5
619	109.4 ± 2.0	89.4	−20.0
665	122.4 ± 10.0	122.1	−0.3
677	133.4 ± 21.3	131.8	+2.4
Hydrogen pressure, 115 mm.			
498	23.1 ± 8.0	18.0	−5.1
577	39.7 ± 2.4	35.3	−4.4
658	65.4 ± 3.5	63.0	−2.4
719	94.2 ± 4.4	91.8	−2.4

Table V tabulates, in the third column, not only the average observed specific diffusion but the deviation of other observed values, for that temperature, from the average. A comparison of the values in the fifth column with these deviations is the essential purpose of the table. As a summary of this comparison, the average deviation of specific diffusion values from their means in Table III A, B and C is 9.8%, while the average deviation of the calculated values from the observed as exhibited in Table V is 7.9%. The calculated results check the observed to within the experimental error.

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[20] The reader should bear in mind that Curves L, R and J are not drawn to the same scale as H.

The *Heat* of Hydrogen Dissociation.—The constant, q, represents the heat of dissociation of the gas within the metal. For hydrogen in nickel this quantity (average for ten different determinations) is 20.8 ± 2.2 kilogram calories. Using data from Lombard's first paper,[3] an average of 29.7 ± 14.1 kilogram calories was found. These values are surprisingly low.

Richardson, Nicol and Parnell's value for the heat of dissociation of hydrogen in platinum was found to be **36.5** kilogram calories. The energy of molecular hydrogen's dissociation is commonly given as 100.0 kilogram calories. Richardson's lower value can be reconciled with this by assuming that platinum's energy of hydrogen-adsorption has reduced hydrogen's energy of dissociation within the metal. Johnson and Larose also found a lower value, 43.2 kilogram calories, for oxygen's dissociation within silver than the usual 160.0 kilogram calories, the heat of dissociation for molecular oxygen. This can be accounted for as was hydrogen's value in platinum.

Extending the same reasoning to the heat of dissociation of hydrogen in nickel requires that nickel's energy of adsorption for hydrogen be greater than that of platinum. The fact that nickel's coefficient of thermal expansion is one and one-half times that of platinum might aid in an explanation if greater expansion could be interpreted to mean greater internal surface for adsorption and so greater activation. This would mean that this heat of dissociation should become less at higher temperatures. **A** preliminary examination of the data for the diffusion of hydrogen through nickel indicates that this last statement is roughly true. A more thorough study of this might prove profitable.

Conclusions

1. Zinc has been shown to be permeable to hydrogen at temperatures between 305° and its melting point.
2. Pure copper, or at least oxygen-free copper, has been shown to be permeable to hydrogen from 500° and above. The hypothesis is advanced that its tendency to become brittle and fissured is due to the development of larger planes of cleavage as the crystal size increases rather than to the reducing action of the diffusing gas.
3. Within the limits of experimental error the diffusion of gases through metals is best related to temperature and pressure by $D = KP^{1/2}T^{1/2}e^{-q/4T}$.
4. It is suggested that more precise technique in this field may lead to a modification of the preceding generalization.
5. The heat of dissociation of hydrogen gas within nickel has been determined as 20.8 ± 2.2 kilogram calories. The "constancy" of this constant has been questioned.

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

SOME REACTIONS OF ATOMIC HYDROGEN

BY H. C. UREY AND G. I. LAVIN[1]

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The preparation and properties of atomic hydrogen have been described by a number of investigators.[2] Langmuir[3] has shown that tungsten filaments at high temperatures cause the dissociation of molecular hydrogen and has used this method to study the reactions of the atomic species with various solids. Wood[4] while working on the Balmer series of the hydrogen spectrum, obtained by passing a high tension electric discharge through moist hydrogen at low pressures, showed that it was possible to remove hydrogen atoms from the discharge tube. He also pointed out that if atomic hydrogen is to be obtained from the tube the hydrogen must be moist; he assumed that the moisture poisoned the walls, thus preventing the catalytic recombination of the hydrogen atoms. Cario and Franck[5] found that hydrogen atoms are formed when a mixture of molecular hydrogen and mercury vapor is illuminated with light of wave length 2536.7 Å., the resonance line of mercury, and Taylor[6] gives an account of an improved method of using the Cario and Franck method. Bonhoeffer[7] using Wood's method has shown that atomic hydrogen reduces a wide variety of metallic oxides and salts and Boehm and Bonhoeffer[8] found that atomic hydrogen reacts with several gases. The reaction of atomic hydrogen with organic compounds has been investigated by Marshall,[9] who was unable to find any reaction between methane and atomic hydrogen. Taylor and Marshall[10] found that atomic hydrogen would react with ethylene to give ethane, and Bates and Taylor[11] found that ethylene probably reacts with atomic hydrogen to give ethyl, C_2H_5, and that there was a marked tendency for higher hydrocarbons to be formed. Recently Wartenberg and Schultze[12] have studied the action of atomic

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[1] This paper and the following are extracts from a dissertation presented by G. I. Lavin to the Faculty of the Graduate School of Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] See Bonhoeffer, "Ergebnisse der Exakte Naturwissenschaften," **1927**, p. 201, for a complete review to that date.

[3] Langmuir, THIS JOURNAL, 44, 860 (1922).

[4] Wood, *Proc. Roy. Soc. London*, **97**, 455 (1920); *ibid.*, **102**, 1 (1923); *Phil. Mag.*, **42**, 729 (1921); *ibid.*, 44, 538 (1922).

[5] Cario and Franck, *Z. Physik*, 11, 161 (1922).

[6] Taylor, THIS JOURNAL, 48, 2840 (1926).

[7] Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

[8] Boehm and Bonhoeffer, *ibid.*, **119**, 385 (1926).

[9] Marshall, *J. Phys. Chem.*, **30**, 1634 (1926).

[10] Taylor and Marshall, *ibid.*, **29**, 1140 (1925).

[11] Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).

[12] Wartenberg and Schultze, *Z. physik. Chem.*, **2**, 1 (1929).

hydrogen on methane, ethane, ethylene and acetylene, and have found no reaction with methane, a catalytic recombination of the atomic hydrogen with ethane and acetylene, and a reaction of atomic hydrogen with ethylene to give ethane. Taylor and his collaborators,[13] have found that other products than ethane are produced if a large excess of hydrogen is not present. The purpose of this investigation was to try the effect of atomic hydrogen on several organic compounds in the solid and gaseous states. Since Wood's method gives atomic hydrogen in the largest amounts, this method was used in its preparation. Also, since water vapor seems to play an important role in the production or the preservation of atomic hydrogen, we have made some preliminary experiments on the active gases coming from a Wood's discharge tube when only water vapor is passed through it. The results of these experiments will be described in the following paper.

Experimental

Figure 1 represents diagrammatically the apparatus used in the work with atomic hydrogen on solid organic compounds. Hydrogen from a tank was led through a cotton wool filter, B, through a water bubbler, C and then to a system of capillaries. D. The T-tube, A, maintained a constant pressure on the incoming gases. The stopcock to which the capillaries were attached was so constructed that connection could be made to *any* one of the four capillaries or so that the system could be cut off entirely from the supply of hydrogen. The rate of flow of hydrogen through the capillaries with one atmosphere of pressure on one side and a few mm. on the other was 12, 22, 40 and 60 cc. per minute of hydrogen measured at atmospheric pressure. From the capillaries the hydrogen passed to the discharge tube, E, which was about a meter in length with the inlet and outlet about 25 cm. apart, and cooled by a water-bath through which water circulated continually. A trap H protected the pumps from water vapor and also served to condense any volatile reaction products. The large stopcock I was used to cut off the apparatus from the pumps. The pumping system consisted of a three-stage Gaede all steel mercury vapor pymp, backed up by a large capacity oil pump; with this arrangement it was possible to pump 60 cc. of hydrogen per minute through the apparatus and still maintain a pressure of about a half mm. of mercury. The pressure in the discharge tube was measured by a McLeod gage connected at a point between the capillaries and the discharge tube. The substances to be exposed to the active hydrogen were placed in the apparatus through the ground glass joint, F. A 2 KVA transformer was

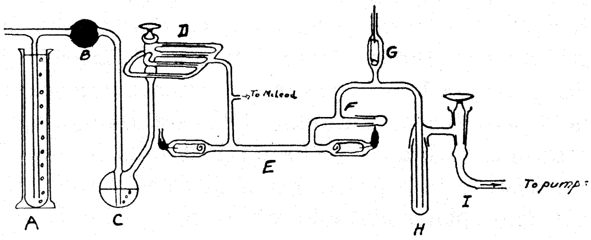

Fig. 1.

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[13] Taylor and co-workers, *Z. physik. Chem.*, **2,449** (1929).

used to excite the discharge. The auxiliary electrode, G, described by Bonhoeffer' was used to clean out the exit tube.

It is well known that active spots may develop on the walls, causing the recombination of the atomic hydrogen, and it was, therefore, necessary to prove the presence of atomic hydrogen at the point where the solid substances were to be placed. This was done before every run by placing a small piece of platinum wire beyond this point, and being certain that the platinum was heated to a red heat before introducing the substances to be investigated. The wire was removed before the substances were introduced.

Reactions with Solid Organic Compounds.—Azoxybenzene was first exposed to the action of the atomic hydrogen; a reduction of the azoxy group to the azo group would be accompanied by a color change from yellow to red, and so would be easy to detect. Azoxybenzene was placed in a porcelain boat about 20 cm. from the discharge tube. When the discharge was turned on there was an immediate change from the yellow azoxy- to the red azobenzene. This change was accompanied by a bubbling and melting of the red mass, and aniline was detected in the trap. Azobenzene was next used and became white, indicating the reduction to hydrazobenzene. Thus we probably have the reduction Azoxybenzene ⟶ Azobenzene ⟶ Hydrazobenzene ⟶ Aniline.

Copaux, Perepot and Hocart[14] have shown that atomic hydrogen will decolorize such dyes as Indigo, Orange II and Safarine T and that the color is partially restored by exposure to atmospheric oxygen. Orange II, Pontamine Diazo Black, Auramine O[15] and Indigo were exposed to the action of atomic hydrogen. The method used in exposing the dyes was to make a paste with a few drops of distilled water; this paste was placed on small glass plates and allowed to dry. The dye-covered plates were then placed in the apparatus (about 20 cm. from the discharge tube) through the ground-glass joint, F (Fig. 1). In every case the dyes immediately turned white. When the white substances were taken from the apparatus and allowed to stand in the air some of the color reappeared, showing that the dyes had been reduced to a stage from which reoxidation to the colored compound could take place and that they had not been entirely destroyed by the reaction with atomic hydrogen. Indigo was immediately reduced to indigo white by the atomic hydrogen. That the white substance formed was indigo white was shown by the fact that it oxidized to the colored compound when dissolved with dilute sodium hydroxide.

Although benzoic acid and acetamide both catalyzed the recombination of atomic hydrogen, we secured no evidence for any reaction between these two substances and the atomic hydrogen. The work on these solid compounds seems to indicate that the atomic hydrogen is only a comparatively mild reducing agent, and that it attacks the more easily reduced groups first.

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[14] Copaux, Perepot and Hocart, *Bull. soc. chim.*, [4] 37, 141 (1925).

[15] These were kindly furnished us by the E. I. du Pont de Nemours Co.

Reaction with Gaseous Organic Compounds.—In order to study gaseous organic compounds the apparatus was modified by placing a 750-cc. bulb between the discharge tube and the ground joint, the reactions being allowed to take place in this bulb. This bulb gave the gases a longer time in which to react and it may also prolong the life of the atomic hydrogen, since Kaplan[16] has shown that the life of atomic hydrogen is decidedly increased when the volume-to-surface ratio of the containing vessel is increased. To this bulb was sealed an inlet for the gases consisting of a capillary stopcock and small flask. The flask was attached to the stopcock by a ground-glass joint so that it could be removed in order to introduce volatile compounds. The rate at which vapors were introduced into the apparatus could be regulated by the size of the capillary and the temperature of the flask. Formic acid was found to catalyze the recombination of the hydrogen atoms. This was indicated by the increased temperature of the tube where the formic acid entered the apparatus. Color tests were secured for formaldehyde; the formic acid used did not give these tests. The amount of formic acid caught by the trap was determined by titrating with sodium hydroxide and it was found that very nearly all of the formic acid which entered the apparatus was recovered. It seems probable that the formic acid may have been decomposed by the hot glass walls to water and carbon monoxide and that the formaldehyde detected was the result of a reaction between carbon monoxide and atomic hydrogen. Bonhoeffer showed that in the case of oleic acid the COOH group is not attacked.

Freshly distilled acetaldehyde was polymerized to paraldehyde, but no further reaction could be detected except that the condensed material had a slightly yellow color, indicating that some decomposition or resinification had taken place. During these tests the bulb developed some active spots which became incandescent when the atomic hydrogen was led in. These glowing points were extinguished by the admission of acetaldehyde and they reappeared when the supply of acetaldehyde was cut off. The acetaldehyde seemed to "poison" these active spots.

It was noticed that when the acetaldehyde was first admitted to the bulb there was a flash of light, and if the supply was suddenly cut off, there was a similar flash. It was found that if just the correct amount of acetaldehyde was allowed to enter the bulb, a continuous glow could be maintained. The light was blue-green in color and when photographed with a small Hilger quartz spectrograph was found to consist of three bands in the region of 4000, 4250 and 4260 Å.; Bonhoeffer and Harteck[17] have found that saturated and unsaturated hydrocarbons react with atomic hydrogen with the emission of bands which lie in this region. Even with

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[16] Kaplan, *Phys. Rev.*, **30**, 639 (1927).

[17] Bonhoeffer and Harteck, *Z. physik Chem.*, **139**, 64 (1928).

a three-hour exposure the bands were too weak to permit exact measurements and all attempts to increase the intensity failed. It was found that the solid acetaldehyde condensed in the trap also glowed under the influence of the active gas, the color being about the same as that given by acetaldehyde in the vapor state.

Summary

The action of atomic hydrogen prepared by Wood's method on some solid and gaseous organic compounds has been studied. It has been found that atomic hydrogen for the most part acts as a rather mild reducing agent, reducing azoxybenzene at least partially to azobenzene and azobenzene partially to hydrazobenzene with aniline as the final product. Certain solid dyes are reduced to colorless compounds which are partially reoxidized to the colored form on exposure to air. Benzoic acid and acetamide catalyze the recombination but are not noticeably reduced.

Atomic hydrogen recombines in the presence of formic acid. A small amount of formaldehyde is produced, probably due to the decomposition of the acid by heat into water and carbon monoxide and the subsequent formation of the aldehyde from carbon monoxide and atomic hydrogen. Acetaldehyde is polymerized to paraldehyde. A faint blue chemiluminescence was observed.

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

REACTIONS OF DISSOCIATED WATER VAPOR

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It is well known that if an electric charge is passed through water vapor at low pressures the Balmer series of hydrogen and the so-called water bands appear with great intensity. Thus it appears that water is dissociated into H and OH in the electric discharge. Also the fact that the OH bands are emitted[1] by the gases leaving Wood's tube as used in the production of atomic hydrogen shows that the OH molecule can be pumped to considerable distances from the discharge tube. It was thought worth while to see whether atomic hydrogen and OH molecules formed by the dissociation of water vapor in an electric discharge could be detected outside the tube.

Experimental

The only change in the atomic hydrogen apparatus described in the preceding paper was the substitution of a flask of water for the tank

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[1] *See* **Bonhoeffer,** *Z. physik. Chem.,* **116,391 (1925).**

of hydrogen and the bubbler C. The oil pump was of the type which permitted the collection of gases coming from the apparatus. An analysis showed that more than two-thirds of the gases leaving the apparatus was hydrogen. Two typical analyses are given below. In the last column is given the excess of hydrogen over that necessary to react with the oxygen to form water.

Total quantity of gas, cc.	O_2, cc.	H_2, cc.	Excess H_2, %
21.50	5.90	15.10	21.85
21.80	6.20	15.60	20.51

Hydrogen peroxide was detected in the water condensed in the trap, which seems to account for the excess hydrogen in the gaseous products. These results are in accord with some old observations of Thompson, who showed that if water vapor is decomposed by an electric spark, an excess of hydrogen over that necessary to react with the oxygen to form water is obtained, and also with those of Kernbaum,[2] who passed a brush discharge through water vapor and found that hydrogen peroxide was formed.

The gases leaving the discharge tube were found to be very active. A strip of platinum exposed to these gases glowed with greater intensity than when exposed to atomic hydrogen produced in the same tube. It was heated almost white hot. From the considerations mentioned in the introduction it seems probable that atomic hydrogen and OH molecules are both present in these gases. The following experiments were carried out to prove the existence of these two constituents.

Evidence for the Presence of Atomic Hydrogen.—Langmuir,[3] Cario and Franck,[4] and Bonhoeffer[5] have shown that atomic hydrogen will reduce copper oxide at room temperatures. A piece of copper gauze was oxidized in the Bunsen flame, part of the gauze being left unoxidized in order to determine whether the active gas was oxidizing or reducing. The gauze was placed in the bottom of a trap, H, as shown in Fig. 1 of the preceding paper, which was about 25 cm. from the discharge tube. The copper oxide was reduced to bright metallic copper and the bottom of the trap became quite warm during the reaction. Evidently the gases are reducing rather than oxidizing in character. A crystal of copper sulfate placed in the apparatus was immediately reduced to the metal. At the beginning of the reaction the crystal appeared to be black, indicating that the salt was probably decomposed into copper oxide and some other product before final reduction took place. The copper was smooth,

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[2] Kernbaum, *Compt. rend.*, **151**, 319 (1910).

[3] Langmuir, This Journal, 44, 860 (1922).

[4] Cario and Franck, *Z. Physik*, 11, 161 (1922).

[5] Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

giving the impression of having been fused. The water condensed in another trap which was surrounded by liquid air gave a test for sulfate. Indigo was exposed to these active gases and as in the case when it is exposed to atomic hydrogen it was reduced to indigo white. Small portions of the solid indigo were torn off and became incandescent. No such violent action was observed in the experiments with atomic hydrogen described in the preceding paper.

The chemiluminescence observed when acetaldehyde was exposed to the action of atomic hydrogen[6] was also observed when acetaldehyde was exposed to these gases. Moreover, mercury exposed to the action of these gases emitted a visible violet light which consisted of the HgH bands and also the 2536 Å. line of mercury. The mercury was placed in the bottom of the trap used to study the reduction of copper oxide; a beaker containing water at about 50° was placed around the trap. As the mercury warmed up the luminous region separated into two parts, one of which traveled slowly up the walls of the trap and the color changed from violet to green. The separation is due to the fact that distillation took place and the mercury condensed in the upper, cooler portions of the trap. As Bonhoeffer has shown,[5] mercury is excited by atomic hydrogen only in the neighborhood of liquid mercury. Thus the separation of the luminous region into two parts is explained. The interesting point in this observation is that atomic hydrogen must have passed through a region containing mercury vapor without exciting the mercury vapor to emit light and without being destroyed by recombination to molecular hydrogen. A quartz window was attached to the side of the trap and a photograph taken with the small Hilger quartz spectrograph. The mercury hydride bands were obtained along with the 2536 Å. line of mercury. All these observations have been made previously when atomic hydrogen alone is present in the exit gases.

Experiments Indicating the Presence of the OH Molecule.—The gas coming from a water discharge tube seems to be even more active than atomic hydrogen. Bonhoeffer was unable to effect the reduction of nickel chloride and iron chloride with atomic hydrogen, but these two salts are reduced to the metal by the gases leaving the water discharge tube.

Olson and Meyers[7] have found that ethylene reacts with atomic hydrogen to form methane, ethane, propane and butane. This suggests that OH molecules might react with ethylene to give an addition product containing oxygen, as, for example, ethyl alcohol or glycocoll. The ethylene was allowed to mix with the active gases coming from the discharge tube and any products resulting were collected in a trap cooled

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[6] Urey and Lavin, THIS JOURNAL, 51, 3286 (1929).

[7] Olson and Meyers, *ibid.*, 49, 3131 (1927).

with liquid air. Blank tests were first run, without passing the discharge through the streaming water vapor. The liquids caught in the trap did not give the iodoform test for alcohol nor did they reduce Fehling's solution. The discharge was then turned on and a similar experiment made.[8] No back diffusion of the ethylene gas took place, for otherwise there would have been a change in the spectrum of the discharge tube, which was not observed. Moreover, simple calculations showed that with the approximately known velocity of the water vapor leaving the discharge tube such back diffusion could not have taken place. The liquid which condensed in the trap had the odor of acetaldehyde, gave the iodoform test and reduced Fehling's solution. This seemed to indicate the presence of acetaldehyde. With the amounts which we were able to secure it was impossible definitely to identify any ethyl alcohol or glycocoll in the reaction products. The presence of the acetaldehyde indicates, however, that some active molecule containing oxygen must he present in the outlet gases.

An attempt was made to prove the presence of OH by taking the absorption spectrum of the gas coming from the discharge tube. No absorption coming from the known band at 3064 Å. was observed. This may not prove the absence of the OH molecule but it does seem to indicate that it must be present in rather small amounts.

Several unsaturated oils such as cottonseed oil, linseed oil, etc., were exposed to the action of the dissociated water vapor. In every case a white solid insoluble in the common organic solvents was obtained. A report of this work will appear in a forthcoming publication.

The authors are indebted to Dr. E. E. Reid for valuable suggestions and criticisms.

Summary

1. Water vapor, dissociated in a discharge tube, gives reactions which are characteristic of atomic hydrogen. From these results we conclude that atomic hydrogen is present in the active gas.

2. Water vapor seems to be more active than atomic hydrogen, in that it will reduce metallic salts which are not reduced with atomic hydrogen.

3. Active gas is prepared from water vapor with greater ease than from hydrogen.

4. It has been indicated that there is another active constituent, probably the OH molecule, present in the active gas.

BALTIMORE, MARYLAND

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[8] The tube where the ethylene entered the apparatus became very warm during the run.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

ABSOLUTE MEASUREMENTS OF THE SURFACE CONDUCTIVITY NEAR THE BOUNDARY OF OPTICALLY POLISHED GLASS AND SOLUTIONS OF POTASSIUM CHLORIDE

BY JAMES W. McBAIN, CHARLES R. PEAKER AND A. MILLICENT KING

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This communication is the result of measurements initiated at Bristol University with W. F. Darke in 1919[1] and continued by R. T. Dale, C. S. Salmon, W. J. Elford and ourselves, subject only to long delays in supply, measurement, remeasurement and replacements of optically polished slits of adhesed glass; it was necessary to carry out the final measurements with slits of poor quality delivered in a damaged condition.[2]

J. Stock[3] found that quartz powder, dropping through nitrobenzene, ether or toluene, imparted a distinct additional conductivity to the system; this he interpreted in accordance with the suggestions of Smoluchowski.[4] Since our work was begun, several investigators found an enhanced conductivity in the presence of powders and other finely divided materials of unknown surface area. Thus Miss Laing[5] found that soap curd conducted better than the mother liquor entrained among the curd fibers; similarly, Fairbrother[6] with quartz glass and carborundum, Stamm[7] with wood fibers, and in particular Briggs[8] with cellulose. All these rendered the existence of excess conductivity in the neighborhood of surfaces extremely likely, but quantitative evaluation would require measurement of the obstruction offered by the fibers as well as the extent and accessibility of the surfaces. Likewise, the origin of such enhanced conductivity, whether due to free mobile ions corresponding to uncovered or unbalanced charges on the interface or due to mere concentration or positive sorption of salt solution in the neighborhood of the interface, remained uncertain. However, another[9] experimental measurement of absolute surface con-

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[1] J. W. McBain and W. F. Darke, "General Colloid Discussion," *Trans. Faraday Soc.*, 16, 150 (1921); *Kolloid-Z.*, 28, 239 (1921).

[2] The last set of glass slits, costing £80, were delivered through the mail, loose in a wooden box without packing.

[3] J. Stock, *Anzeiger Akad. Wiss. Krakau*, Reihe **A**, 635 (1912); 131 (1913); 95 (1914).

[4] M. Smoluchowski, *Physik. Z.*, 6, 529 (1905).

[5] M. E. Laing and J. W. McBain, *J. Chem. Soc.*, *117*, 1506 (1920).

[6] F. Fairbrother and H. Mastin, *ibid.*, 125, 2319 (1924); F. Fairbrother, *ibid.*, 125, 2495 (1924).

[7] A. J. Stamm, "Colloid Symposium Monograph," 4, 253 (1926).

[8] D. R. Briggs, *J. Phys. Chem.*, 32, 641 (1928).

[9] J. W. McBain and C. R. Peaker, *Proc. Roy. Soc. London*, **125A**, 394 (1929). A further communication (*J. Phys. Chem.*) will deal with results which we have obtained in a much simplified, easily made apparatus, permitting rapid comparisons of surface conductivity and quantitative determinations of its absolute amount.

ductivity leaves little room for doubt that the conductivity is due to the mobile ions corresponding to those attached to the interface. These experiments measured the conductivity in the neighborhood of the monomolecular film of fatty acid on water and showed that such a film is composed to the extent of about one-ninth of fatty ions, the remaining molecules being undissociated. Hence the conductivity is due to the free mobile hydrogen ions corresponding to the fatty ions in the thin film. Once any absolute measurements have been made, it is easy to standardize other experiments involving the same materials.

The experiments of Darke and the subsequent ones of Dale and Salmon were carried out with fine capillaries of fused silica. To magnify the conductivity, these were mounted in a large group in parallel, passing through a partition of shellac melted on and around them so that only their ends projected. Enhanced conductivity was observed, but such measurements could not be regarded as definitive, owing to the possibility of a leak or defective insulation between the tubes and the shellac. This was obviated by making two partitions of shellac with an accessible air gap between, the whole being enclosed in glass tubing. This arrangement yielded low values or excess conductivity and was discarded because of the impossibility of ensuring that the interior of the quartz surfaces had not become contaminated by the necessary manipulations. These results will be referred to in the discussion.

The next extensive series was made by Elford, using a pile of fifteen parallel quartz plates with optically polished surfaces. They were held in a rectangular cell made of optically polished glass, adhesed to form a unit. This was made by A. Hilger, Ltd. (London), and the dimensions (supplied at a much later date in place of those first communicated) were determined by them in a specially developed interferometer with a probable error of only 4000 Å. The results were definitely positive, but the method was ultimately abandoned on account of the difficulty of accurately evaluating dead spaces between the plates and cell, especially with the slight ledges necessary to hold the quartz plates in "position." The quartz plates were piled horizontally to minimize the chance that an optically polished edge might touch a true surface and introduce comparatively large resistance. The results are given later.

The next design made use of during the past six years (whenever available) consisted of a single rectangular slit with optically polished surfaces in a flat piece of glass one inch square. The first three slits, made by Mr. C. Ord of Adam Hilger, Ltd., were very satisfactory, and the dimensions of the slit were known to about one-eighth of the wave length of light. Unfortunately cracks gradually extended from one or more of the adhesed surfaces of the slits during the series of measurements made with them. An anonymous description of the mode of manufacture which appeared in *Nature*[10] may be quoted as follows: "The thickness of a piece of plain parallel quartz some $1^{1}/_{4}''$ X $1^{1}/_{4}''$ X $^{1}/_{8}''$ was being measured on a Michelson interferometer. The half coating of silver had been removed from one of the mirrors of the instrument, and the specimen was then 'contacted on' to this mirror so as to cover one-half of it. The whole was then half silvered, and the distance between the two surfaces was measured in air. What appeared to be a slight scratch in the center of the specimen was in reality a slit in the glass, of width only 16 wave lengths of light (λ 5461). This slit was made in the manner illustrated in the accompanying diagram (Fig. 1). It will be seen that the quartz plate was in reality built up of four pieces, all accurately finished with extreme accuracy. Starting with 1, 2 and 3 were contacted on and heated sufficiently to make these three join up into one piece, but, of course, not too much, or the optical perfection of the surfaces would be spoiled. The protruding edges of 2 and 3 where they meet 4 were then ground and polished so that they extended beyond 1 a distance equal only to 16 wave lengths. This distance was measured with the Michelson interferometer, and then 4 was contacted on and the heating process repeated."

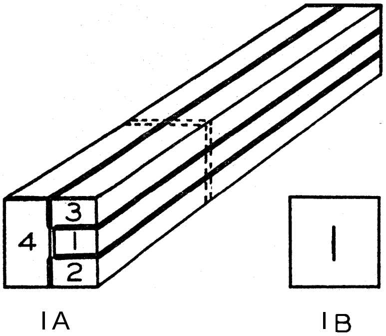

Fig. 1.—1A. Method of preparing slits by "adhesion" of optically polished glass surfaces. The dark lines show the surfaces which have been heated until they "adhered" or united. 1B. Cross section of glass showing slit.

These slits were actually made from four pieces of glass about 10 cm. long so that a number of cross sections could be cut, yielding slits of identical dimensions. At a later date no more of this batch could be supplied, and, although one of us went through the measurements of the glass pieces for the final batch at the factory, the slits actually supplied were of different dimensions which could, of course, no longer be determined interferometrically. The widths of the slits were therefore determined by means of a microscope fitted with a calibrated eyepiece scale, or with a calibrated micrometer eyepiece. Various objectives and eyepieces were used (both Leitz and Zeiss). Measurements were made at intervals of 0.5 to 1.0 mm. along the slit. The lengths of the slits were determined with a traveling microscope, reading to 0.001 mm., the scale of which had been calibrated. The thicknesses of the slits were determined (1) by examination at intervals along the edges of the block with a microscope fitted with a calibrated eyepiece scale, or with a calibrated micrometer eyepiece; (2) by examination at intervals around the edges of the block with a

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[10] *Nature*, **112**, 223 (1923).

traveling microscope; (3) by means of a micrometer caliper, reading to 0.0001 in.

The dimensions obtained by these methods agreed fairly well with those given by Hilger for slits Nos. 1 and 2, but not for the later slits Nos. 4, 5, 6, 7 and 10, the results for the widths of the narrow slits (Nos. 4, 6, 10) being about 10% lower than those of Hilger and about 2% lower for the wider slits (Nos. 5, 7). These were just about the differences Hilger stated might exist due to sagging of the glass, hence the microscopic measurements have been taken as being correct for these slits, while Hilger's measurements have been used for slits Nos. 1 and 2. According to a statement by Hilger, the narrower slits (4, 6, 10) were all cut from the same block, and the wider slits (Nos. 5, 7) from another. It was decided, therefore, that the best procedure would be to average all the values obtained for the widths of the narrower slits (and similarly for the wider slits) and use this average value as the width of all the narrower slits (and similarly for the wider slits) instead of the average values obtained from the measurements of each slit alone. Table I records the dimensions of the slits which have been used in this investigation.

TABLE I

DIMENSIONS OF SLITS

Slit No.	Width, mm.	Length, mm.	Thickness, mm.	Observer
S	0.00939	10.000	0.983	Hilger
1	.0344	10.03	...	Hilger
	.0337	10.10	0.999	King
2	.00634	10.06	...	Hilger
	.00667	10.11	1.001	King
4	.0125	10.01	1.066	Peaker
6	.0125	10.01	1.058	Peaker
10	.0125	10.01	5.014	Peaker
	(.014)	(10.00)	...	Hilger
5	,0567	10.02	1.033	Peaker
7	.0567	10.02	2.101	Peaker
	(.058)	(10.00)	...	Hilger

The accuracy of the final values obtained in this investigation depends greatly on the accuracy with which the dimensions of the slits are known. The possibility of error is greatest in the widths of the slits, since this is the smallest dimension; we estimate that it is probably known to within 2% for the narrower slits used and within 0.5% for the wider slits. The error in the lengths of the slits is probably not over 0.1% and in the thicknesses not over 0.3%.

Procedure for Cleaning Cells and Slits.—The electrode arms of the "main cell" were thoroughly cleaned with nitric acid (1:1), conductivity water, distilled alcohol and distilled ether. Mercury for the electrode arms was cleaned by allowing it to stand in contact with nitric acid (1:1) for a short time, washing with distilled water and filtering through pin-holes in filter paper until clean and dry.

The main cell was cleaned thoroughly with cold dichromate–sulfuric acid mixture and thoroughly rinsed with conductivity water, distilled alcohol and distilled ether. Then it was rinsed out with distilled alcohol and conductivity water. The optically polished "central cell," previously used by Elford to hold quartz plates, was subjected to similar treatment before use.

The glass blocks containing the slits were cleaned externally with dichromate mixture, rinsed with conductivity water, and rubbed lightly with a clean cloth dipped in distilled alcohol. (Treatment with dichromate mixture was omitted in the case of slits Nos. 1 and 2.) After assembling the cell, the slits were cleaned as follows. The cell was filled with fresh dichromate mixture and this drawn back and forth through the slit by applying suction. Then the cell was rinsed out thoroughly in turn with conductivity water, distilled alcohol, distilled ether, distilled alcohol and conductivity water, suction being used to draw the liquids through the slit. (Treatment with dichromate mixture was omitted in the case of slits Nos. 1 and 2.)

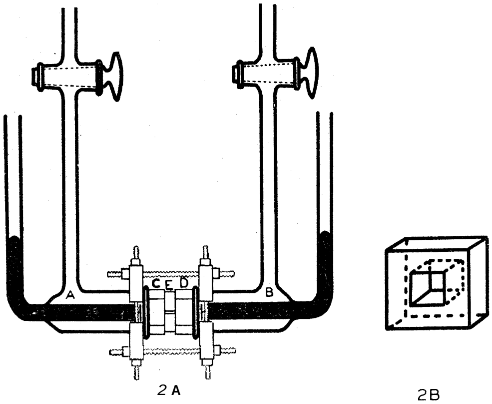

Fig. 2.—2A. The conductivity cells. 2B. Central cell. one is placed on each side of the slit.

The Conductivity Cells.—The type of cell used for measuring the conductivity of potassium chloride solutions in glass capillaries is shown in Fig. 2. It consists of three parts: (1) the two half cells (A, B) containing the electrodes designated as "main cell"; (2) two glass blocks (C, D) about 1 inch square with an opening through them about 1.3 cm. square designated as "central cell"; (3) a glass block (E) containing the optically worked capillary slit. (In some of the measurements made by one of us, the central cell was not used) These various parts are then clamped into the positions shown in the diagram. The clamp was made of square ebonite frames. pulled toward each other by four brass screws at the outside corners, the ebonite being separated from the glass by thick rubber tubing.

In the earlier work a water thermostat was used; the later results were obtained with a thermostat filled with Transil Oil, as used by Grinnell Jones and R. C. Josephs.[11]

The conductivity measurements were made by the method of Kohlrausch, using the improved apparatus designed by Washburn[12] and supplied by Leeds and Northrup. (Some modifications were made in the apparatus used by one of us (C. R. P.) to conform with the recent work of Jones and Josephs.[11] Instead of the fixed ratio slide wire described by them, a Kohlrausch drum-type slide wire (Leeds and Northrup) was used; the grounding resistance was another slide wire of the same type. Since most of the readings were taken at the center of the wire, this arrangement is equivalent to that of Jones and Josephs.) The slide wire was carefully calibrated by the method of Strouhal and Barus,[13] and the necessary corrections were applied. The resistance box was of the five decade type, supplied by Leeds and Northrup; coils of 1000 ohms resistance and

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[11] G. Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928).

[12] E. W. Washburn and J. E. Bell, *ibid.*, **35**, 177 (1913).

[13] A. Findlay, "Practical Physical Chemistry," Longmans, Green and Co., London, 4th edition (1923), p. 154.

above were of the Curtis design. Variable air condensers were shunted across the resistance box. The balance point of the bridge was determined by the use of a set of tuned telephones (one of us (C. R. P.) used a one-stage vacuum tube amplifier in conjunction with the telephones). Alternating current was supplied to the bridge from a Vreeland oscillator at a frequency of 1000 cycles per second (or, by one of us (A. M. K.), from a high frequency generator, or vacuum tube generator).

Preparation of Potassium Chloride Solution.—Various types of stills were used for the preparation of conductivity water,[14] but the conductivity of the water obtained was rarely better than 0.7 X 10^{-6} mhos at 25° and averaged about 1.0 X 10^{-6} mhos at 25". The water was collected and stored in flask.: of Jena glass, which had been thoroughly cleaned with dichromate mixture and which were steamed out each time before use. Correction for the conductivity of the solvent has been made in the tables of data which follow.

The potassium chloride used was Kahlbaum's "for analysis, with guarantee." It was heated in a clean quartz or porcelain dish over a hot Bunsen flame until all crackling ceased and was allowed to cool in a desiccator over phosphorus pentoxide. It was kept in the desiccator at all times except for brief periods when solutions were being made up.

The solutions of potassium chloride were made up by the weight method, the details of which are described by Kraus and Parker.[15] The amount of potassium chloride required was weighed out onto a clean, dry watch glass and transferred to a clean flask (just previously steamed out and rinsed with conductivity water) through a clean funnel (just previously rinsed with conductivity water). The residue on the watch glass and funnel was then rinsed into the flask with conductivity water and the necessary amount of conductivity water added to the flask. The amount of solution was determined by substitution weighing, and from the data the exact concentration of the solution could be obtained. The solution was then well shaken and allowed to stand for several hours before use. In practically every case freshly made solutions were used.

Procedure in Making Determinations of the Specific Conductivity of Potassium Chloride Solutions in Slits.—After assembling and cleaning the conductivity cell as previously described, it was rinsed out three or four times with the most dilute solution to be used (0.001 N potassium chloride), suction being used to draw the solution through the capillary. The cell was then filled with this solution and placed in the thermostat. Usually about half an hour was allowed to elapse before beginning measurements. The resistance of the cell was measured at intervals until a series of constant resistances over a period of, say, one hour, were obtained. The solution was then drawn back and forth through the slit by suction several times and measurements continued until the resistance was again constant. This was repeated several times and the mean of all the constant values for the resistance of the cell taken.

The solution was then emptied out and the cell rinsed two or three times with fresh samples of solution; it was filled again and placed in the thermostat ready for a second series of measurements. Three such independent fillings, giving agreeing results, were considered sufficient; in later work two fillings giving agreeing results were accepted.

After finishing a series of experiments with one concentration, the cell was rinsed with the next most concentrated solution, suction being used as previously; then it was filled and the above procedure repeated. During the transition from 0.001 *N* to 1 N solution the cell was not taken apart.

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[14] C. A. Kraus and W. B. Dexter, THIS JOURNAL, 44,2468 (1922); G. D. Bengough, J. M. Stuart and A. R. Lee, *J. Chem. Soc.*, 2156 (1027).

[15] C. A. Kraus and H. C. Parker, THIS JOURNAL, 44,2422 (1922).

The following tables record the results which have been obtained in this investigation.[16] The first column gives the actual concentration of the solution used. The second column gives the resistances in ohms for each individual experiment. The values in the third column are the means of the values in Col. 2 for each concentration, corrected for the conductivity of the solvent and also corrected to round concentration (in making this slight correction, specific conductivity is assumed to be a linear function of concentration).

TABLE II

RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN MAIN CELL AND CENTRAL CELL AND SLIT S AT 2500 ± 0.02°

Concn., normality at 18° C.	0.01	0.1
Observed resistance, ohms	115,000 115,300	13,440
Corr. mean resist., ohms	115,150	13,440

TABLE III

RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN MAIN CELL AND CENTRAL CELL AND SLIT NO. 1 AT 25.00 ± 0.02°

Concn. (normality at 18°)	Observed resistance. ohms				Corr. mean resistance, ohms
0.000998	201,211	201,096	200,818		200,640
.001995	106,482	107,286	106,993	106,571	106,560
.010003	(23,743)	23,642.5	23,643	23,632.4	23,646
.10002	(2,613.5)	2,603.1	2,600.4	2,602.2	2,602.4
.9998	(301.13)	300.49	300.59	300.11	300.33

TABLE IV

RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN MAIN CELL AND CENTRAL CELL AND WIDE SLIT NO. 1 AND NARROW SLIT NO. 2 AT 25.00 ± 0.02°

Concn. (normality at 18°)	Observed resistance, ohms					Corr. mean resistance, ohms
0.000998	(898,711)	873,714	874,357	892,300		878,360
.001984	(553,996)	(539,721)	490,680	493,613		488,210
.010006	122,067	(1 18,860)	121,914	(124,574)	(127,692)	
	122,201	(120,300)	(127,148)	122,195	(121,369)	122,160
.1001	(14,791)	(14,616)	14,049	13,922		13,910
.9954	(1,673.2)	1,671.5	1,666.2			1,661.2

TABLE V

RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN MAIN CELL AND NARROW SLIT No. 4 AT 24.91–24.92°

Concn. (normality at 18°)	Observed resistance, ohms				Corr. mean resistance, ohms
0.001004	(552,310)	582,130	600,280	595,900	599,270
.001996	311,010	315,970			317,920
.001998	322,640				
.009995	75,408	74,950	74,662	74,612	74,863
.1000	7,435.0	7,443.2	7,448.5		7,442.9
.9975	854.97	859.77	858.35	856.62	855.26

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[16] The data for slits No. S, No. 1, and No. 1 and No. 2 together were obtained by Miss King; the remainder were obtained by Mr. Peaker.

TABLE VI

RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN MAIN CELL AND WIDE SLIT NO. 7 AND NARROW SLIT NO. 4 AT 24.91–24.92°

Concn. (normality at 18°)	Observed resistance, ohms					Corr. mean resistance, ohms
0.000992	509,750	873,720	816,600	803,340	839,840	820,640
.000997	751,050					754,900
.002002	417,600	420,700	424,290			423,220
.010026	92,965	92,402	91,174			92,534
.09999	10,050	10,041	10,031			10,041
.9975	1,160.1	1,159.3	1,157.0			1,155.9

TABLE VII

RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN MAIN CELL AND WIDE SLIT NO. 7 AT 24.91–24.92'

Concn. (normality at 18°)	Observed resistance, ohms					Corr. mean resistance, ohms
0.000997	242,670	242,000	(225,630)	245,660	247,220	245,360
.002001	127,900	127,580	127,900			128,230
.009998	27,363	27,694	27,579			27,557
.1000	3,060.1	3,040.0				3,050.2
3965	354.69	354.90	354.33			353.40

TABLE VIII

RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN MAIN CELL AND CENTRAL CELL AND NARROW SLIT NO. 4 AT 25.01–25.02°

Concn. (normality at 18°)	Observed resistance, ohms		Corr. mean resistance, ohms
0.001006	584,940		591,430
.010012	64,560	66,351	65,570
.9821	851.36	857.50	839.15

TABLE IX

RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN MAIN CELL AND CENTRAL CELL AND NARROW SLIT NO. 10 AT 25.01–25.02'

Concn. (normality at 18°)	Observed resistance, ohms			Corr mean resistance, ohms
0.01000	300,000	313,910	310,680	312,500
1.0020	4,244.0	4,237.2		4,249.1

TABLE X

RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN MAIN CELL AND CENTRAL CELL AND WIDE SLIT NO. 5 AT 25.01°

Concn. (normality at 18°)	Observed resistance, ohms			Corr. mean resistance, ohms
0.001001	140,850	142,370		141,830
.010004	15,998			16,015
.1006	1,760.8	1,760.8		1,771.4
.9651	(220.77)	211.53	211.50	204.45
.9902	207.12			

TABLE XI

RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN MAIN CELL AND CENTRAL CELL AND NARROW SLIT NO. 6 AT 25.00–25.01'

Concn. (normality at 18°)	Observed resistance, ohms			Corr. mean resistance, ohms
0.000992	532,110			529,710
.010004	65,372	65,450		66,214
.010014	66,683	66,979		
.1006	7,464.2	7,461.0	7,435.2	7,498.3
.9821	978.00	976.40		957.40
.9990	956.82	955.28		

Time Effect.—In the case of the dilute solutions, drawing the solution in the cell back and forth through the slit after equilibrium had been established (as shown by constant resistances over a period of time) generally caused the resistance to rise somewhat, and then it fell off with time until a value comparable with the previous value had been reached, after which the resistance remained fairly constant. This is what one would expect if the excess conductivity is ascribed to the mobile ions existing free in the solution. For the more concentrated solutions (0.1–1.0 N), drawing the solution through the slit caused slight, irregular variations. In the preliminary work of Dale, Darke and Salmon it was found that a new capillary on its first filling showed diminished conductivity (due to sorption) which was replaced by enhanced conductivity (ordinary bulk conductivity plus conductivity of mobile ions) upon drawing further solution through the capillary.

Precision of the Recorded Data.—For 0.01 to 1.0 N solutions the values averaged to give the recorded value for each experiment in the preceding tables do not differ by more than 0.1–0.2% from this value. The mean obtained for each concentration (Col. 3 of tables) is probably correct to 0.1–0.2%. For dilute solutions (0.001-0.002 N) the values averaged to give the recorded value for each experiment are within 0.5% of the mean. The mean values for each concentration are probably correct to about 1%.

Specific Conductivities of Potassium Chloride Solutions in **Bulk.**—Table XII gives the values of the specific conductivities of the potassium chloride solutions used in this investigation, as obtained from the literature.

TABLE XII

SPECIFIC CONDUCTIVITIES OF POTASSIUM CHLORIDE SOLUTIONS IN BULK

Concn. (normality at 18°)	0.001	0.002	0.01	0.1	1.0
Sp. cond. at 25°, mhos	0.0001466	0.0002907	0.0014104	0.012877	0.11169
Investigator	Kohlrausch	Kohlrausch	Parker and Parker	Parker and Parker	Parker and Parker

In Table XIII are given the calculated resistances of the various potassium chloride solutions in the slits which were used in this work. These values were obtained from the dimensions given in Table I and the specific conductivities in Table XII.

TABLE XIII

CALCULATED RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN SLITS (ASSUMING NO SURFACE CONDUCTIVITY)

No. of slit	0.001 N	0.002 N	0.01 N	0.1 N	1.0 N
S			74,223	8,129.4	
1	197,500	99,595	20,528	2,248.4	259.23
2	1,070,600	539,880	111,280	12,188	1,405.2
4	581,150	293,070	60,406	6,616.0	726.80
6	576,790	290,870	59,953	6,566.4	757.08
10			284,120	31,119	3,587.8
5	124,030	62,546	12,892	1,412.3	162.79
7	252,260	127,210	26,220	2,871.9	331.11

In order to decide whether there is any change in the specific conductivity of potassium chloride solutions in capillaries compared with that measured in bulk, it is necessary to determine from the observed resistances of main cell, central cell and slit the resistance of the slit alone. Comparison of the resistances so obtained with those given in Table XIII will then show whether or not there is any change in the conductivity when measured in capillaries.

In the early stages of this investigation it was thought that by subtracting the resistance of the main cell and central cell, measured separately, from the resistance of main cell, central cell and slit, the result would be the true resistance of the solution in the slit; but when this was done, a decrease in the specific conductivity was obtained for the more concentrated solutions, and only for the dilute solutions was an increase observed. This decrease in conductivity observed in the concentrated solutions was evidently to be ascribed to a "pinch" effect,[17] operating in all concentrations and due to bending of the lines of current flow through the slit, and equivalent to a series resistance. In other words, the whole cross section of the main cell and central cell is not available for carrying current in the immediate neighborhood of the slit. A similar "pinch" effect operated in the experiments of Elford, referred to previously.

In order to eliminate the "pinch" effect, it was decided to use two slits together; in this way the resistance of one slit (say No. 1), obtained by

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[17] We satisfied ourselves with ad *hoc* measurements that the "pinch" effect not only exists but that its magnitude has been correctly deduced. For this purpose we used, for example, a fine platinum wire of the same diameter in place of the slit and found that the total resistance between the electrodes was about equal to the resistance between the central platinum wire and either of them. The resistance between the central wire and one of the electrodes was again doubled by putting a glass plate behind the platinum wire. In other experiments the half cell was closed with a paraffin block, into the surface of which a platinum wire had been crushed and then platinized, and a similar large "pinch" effect was found.

subtraction of the observed resistance of slit No. **2,** main cell and central cell from that for both slits, main cell and central cell would be independent "pinch" effect. Since the slits used for this purpose were not of the same width (one being roughly five times the width of the other), the assumption is made in such a calculation that the "pinch" effect is the same for a slit, say, 0.05 mm. wide as for one only 0.01 mm. wide. In the early part of this investigation the truth of this assumption could not be checked because we had difficulty with cracking of the glass blocks containing the slits; later data, obtained on slits which were not cracked, showed that the assumption was not valid. If we consider the data for slits No. 5 and No. 6, this will be quite apparent.

For 1.0 N solution the resistance of main cell, central cell and slit No. 5 is 204.45 ohms (Table X). If we assume that for this concentration surface conductivity is negligible compared to bulk conductivity and consider that the resistance of the slit itself is 162.79 ohms, as calculated in Table XIII, then the "total effective resistance" of the main cell and central cell is 41.66 ohms. This is the sum of the "pinch" resistance and the true resistance of the main cell and central cell, measured separately. Since the measured resistance of the latter is 14.14 ohms, the former is 27.52 ohms.

Similarly, considering the data for main cell, central cell and narrow slit No. 6 for 1.0 N solution, we find the measured resistance of this combination to be 957.40 ohms (Table XI), while the resistance of the slit itself is 757.08 ohms (Table XIII). The "total effective resistance" of the main cell and central cell is then 200.32 ohms, and the "pinch" resistance is 186.18 ohms.

The ratio of the "total effective resistance" of the main cell and central cell in the two cases is 200.32/41.66 or 4.81; the ratio of the widths of the slits, which is the only dimension which need be considered, is 0.00567/0.00125 or 4.53. Thus, as a first approximation we may say that the "total effective resistance" of the main cell and central cell is inversely proportional to the width of the slit; the "pinch" resistance, on the other hand, appears to be an exponential function of the width.

Considerable difficulty was encountered in evaluating some of the results, owing to the fact that cracks developed, radiating from the slit, during the course of the experiments. Since the cell was not dismantled during the transition from 0.001 N to 1.0 N solution, it is difficult to say where the cracks first developed and to what extent. However, it seems very probable that the conductivity of such cracks is negligible compared to the conductivity of the solution in the slit itself. Under a microscope, using very high magnification, the crack appears only as a line, whose width cannot be estimated, while the slit covers about $^1/_6$ of the field (in the case of the narrow slit No. 4, for example).

It seems best, therefore, to include any effect of the crack in the term which is called the "total effective resistance" of the main cell and central cell, rather than attempt to make a special correction term for this effect. The following pages give typical methods of calculating the results.

1. Method of Calculating the Results for Slits Nos. **1, 5, 6 and** 10 (Tables **III, IX, X** and **XI**).—For narrow slit No. 6 (Table XI) the resistance of main cell + central cell + slit No. 6 for 1 *N* solution, 957.40 ohms, less the calculated resistance of the slit for 1 *N* solution, 757.08 ohms, leaves the "total effective resistance" of main cell + central cell for 1 N solution equal to 200.32 ohms. Now the "total effective resistance" must be proportional only to the specific resistance of the solution for a given cell and slit. Hence the "total effective resistance" of the main cell + central cell for 0.001 *N* solution is $(200.32 \times 0.11169)/0.0001466 =$ 152,620 ohms. But the resistance of the main cell + central cell + slit No. 6 for 0.001 N potassium chloride was 529,710 ohms, leaving for the resistance of the slit alone 377,090 ohms. The resistance of the slit as calculated from its dimensions and specific conductivity (Table XIII) is 576,790 ohms. The percentage increase in specific conductivity for 0.001 N potassium chloride within the slit is then

$$\left(\frac{1/377{,}090 - 1/576{,}790}{1/576{,}790}\right) \times 100 = \left(\frac{576{,}790 - 377{,}090}{377{,}090}\right) \times 100 = 52.96\%$$

The specific conductivity of a 0.001 N solution in bulk is 0.0001466 mho at 25.00°. Hence the conductivity due to the surface would be 52.96% of 0.0001466 mho or 0.00007764 mho, if 1 cc. of 0.001 N potassium chloride solution were to be confined in a cell, the area of whose walls bore the same ratio to the volume as the area of the actual slit did to the volume of the slit.

It is essential to calculate the surface conductivity in absolute units. Volume conductivity is always expressed by specific conductivity, that is, the conductivity in reciprocal ohms of a cube of solution placed between parallel electrodes 1 cm. square and 1 cm. apart. Similarly, we must invent a specific surface conductivity in two dimensions instead of three (as regards the actual surface area), defining it as the conductivity in reciprocal ohms between two parallel electrodes 1 cm. long, placed 1 cm. apart on the surface. The surfaces in our slits conform to this requirement in that they are parallel to the lines of current flow. As long as the volume and area are varied in the same proportion, the ratio between volume and surface conductivity will remain constant. Hence from the determination given above, since the area of slit No. 6 was 1601.6 times its volume in cc., the specific conductivity of one square centimeter is $0.00007764/1601.6 = 4.85 \times 10^{-8}$ mhos.

The value for the "total effective resistance" just calculated for the uncracked slit No. 6 had to be used for the results of Tables V, VII and

VIII. Slit No. 4 (Table VIII) evidently cracked before the measurement of 1.0 N potassium chloride, although the results for 0.001 N and 0.01 N agree with Table XI. For Table V the "total effective resistance" for 1.0 N potassium chloride is 242.58 ohms, obtained by multiplying the 200.32 ohms by that for the main cell (92.46) in Table V divided by that for the main cell + central cell (76.35) in Table VIII. Again for Table VII, the "total effective resistance" of the main cell for 1.0 N potassium chloride is $(242.58 \times 22.29)/200.32 = 26.38$ ohms; but slit No. 7 had become so badly cracked that the conductivity even of 1.0 N potassium chloride was slightly increased. Hence the volume conductivity of the crack had to be taken into account, and the surface conductivity of dilute solutions was apportioned between crack and slit in the ratio of their lengths.

For Table VI using wide and narrow slits, No. 7 and No. 4 together, the total effective resistance was taken as the mean of the two separately. Then the resistances within each slit were obtained by subtracting the values for the separate slits from the value of the two slits together. Therefore, the surface conductivities are both low on account of the neglected "pinch" resistance between the slits, the wide slit being most affected.

In Table II the original slit No. S was broken after measuring 0.1 N potassium chloride. Assuming the surface conductivity to be of negligible influence in 0.1 N in place of 1.0 N potassium chloride, the calculation gives 7.51×10^{-8} mhos per sq. cm. for the surface conductivity in 0.01 N potassium chloride. Based upon 1.0 N potassium chloride, this would have been a few per cent. higher, but it is in good agreement with the later work.

The earlier work of Dale with fused silica tubes and of Elford with plates of quartz is calculated in the same way. Dale's results (1921) are given for the last three cells he used. With 0.01 N the increased conductivity observed was 1.2 and 1.4%, corresponding to 16.1 and 17.2 X 10^{-8} mhos per sq. cm., respectively. That for 0.002 N was 2.7% or 3.6 X 10^{-8} mhos. The results with quartz plates for higher concentrations are omitted on account of the magnified experimental error. For 0.001 and 0.002 N potassium chloride the increased conductivity was 11.4 and 8.2%, and the specific surface conductivity was 3.9 and 5.6×10^{-8} mhos, respectively.

The data for slit No. 2 alone are omitted because of a wide crack which caused the 1.0 and 0.001 N potassium chloride solutions to exhibit an apparent increase of 42 and 93%, respectively. The difference, 51%, corresponds to a specific surface conductivity of 2.4 X 10^{-8} mhos.

Tables XIV and XV present the evaluation of the results by the methods just described, showing the percentage increase ascribable to surface conductivity and the magnitude of the surface conductivity in absolute units.

TABLE XIV

PERCENTAGE INCREASE IN SPECIFIC CONDUCTIVITY OF POTASSIUM CHLORIDE SOLUTIONS IN NARROW GLASS SLITS AND THE SPECIFIC SURFACE CONDUCTIVITY DEDUCED

Concn. (normality at 18°)	Total resist.	"Effective resistance"	Resist. of slit. Obs.	Resist. of slit. Calcd.	Increase, %	Sp. surface cond., mhos/cm.^{2} $\times 10^8$
Narrow slit No. 6 (from Table XI)						
1.0	957.40	200.32	757.08	757.08	...	...
0.01	66,214	15,863	50,351	59,953	19.07	16.8
.001	529,710	152,620	377,090	576,790	52.96	4.85
Wide slit No. 5 (from Table X)						
1.0	204.45	41.66	162.79	162.79	...	...
0 1	1,771.4	361.3	1,410.1	1,412.3	0.16	5.66
.01	16,015	3,299	12,716	12,892	1.38	5.50
.001	141,830	31,740	110,090	124,030	12.66	5.23
Narrow slit No. 10 (from Table IX)						
1.0	4,249.1	661.3	3,587.8	3,587.8	...	...
0.01	312,500	52,370	260,130	284,120	9.22	5.13
Narrow slit No. 4 (from Table VIII)						
1.0	839 15	200.32	......	......	...	...
0.01	65,570	15,863	49,707	60,406	21.52	18.97
.001	591,430	152,620	438,810	581,150	41.56	3.81
Narrow slit No. 4 (from Table V)						
1.0	855 26	242.58	......	......	...	...
0.01	74,368	19,254	55,614	60,406	8.62	7.60
.002	317,920	94,713	223,207	293,070	31.29	5.68
.001	599,270	185,240	414,030	581,150	40.36	3.63
Wide slit No. 7 (from Table VII)						
1.0	353.40	26.38	......	......	...	...
0.1	3,050.2	228.8	2,821.4	2,871.9	0.34	13.43
.01	27,557	2,089	25,468	26,220	2.95	11.73
.002	128,230	10,135	118,095	127,210	7.72	6.33
.001	245,360	20,098	225,262	252,260	11.99	4.95
Narrow slit No. 4 (from Tables VI and VII)						
1.0	1,155.9	134.48	......	......		...
0.01	92,534	10,649	56,417	60,406	7.07	6.23
.002	423,220	51,670	253,450	293,070	15.63	2.84
.001	754,900	102,460	427,180	581,150	36.04	3.30
Wide slit No. 1 (from Table III)						
1.0	300.33	41.10	259.23	259.23		...
0.1	2,602.4	356.5	2,245.9	2,248.4	0.11	3.08
.01	23,646	3,255	19,391	20,528	5.86	1.80
.002	106,560	15,790	90,770	99,595	9.72	6.14
.001	200,640	31,310	169,330	197,500	16.64	5.30

TABLE XV

PERCENTAGE INCREASE IN SPECIFIC CONDUCTIVITY OF POTASSIUM CHLORIDE SOLUTIONS IN NARROW GLASS SLITS AND THE SPECIFIC SURFACE CONDUCTIVITY DEDUCED

Concn. (normality at 18°)	Total resist.	"Effective resist."	Resistance of: Both slits (measured)	Slit No. 4 (Table XIV)	Slit No. 7 (by diff.)	Slit No. 7 (calcd.)	Increase, %	Sp. surface cond., mhos/cm.^{2} × 10^8
Wide slit No. 7 (from No. 4 and No. 7 together, Table VI and slit No. 4, Table V)								
0.001	754,900	102,460	652,440	414,030	238,410	252,260	5.81	2.4[a]
				Slit No. 1	Slit No. 2	Slit No. 2		
Narrow slit No. 2 (from No 1 and No 2 together, Table IV, and slit No 1, Table III)								
1 0	1,661 2	3 2	1,664 4	259 2	1,405 2	1,405 2	..	..
0 1	13,910	28	13,882	2,245 9	11,636	12,188	4 74	2 0
.01	122,160	253	121,190	19,391	102,520	111,280	8 55	4 0
002	488,210	1,229	486,980	90,770	396,210	539,880	36 26	3 3
.001	878,360	2,438	875,920	169,330	706,590	1,070,600	5152	2 4

[a] Plus conductivity offset by not allowing for "pinch" between slits.

Results and Discussion

In Table XVI are collected the values obtained for the specific surface conductivities, including those of Dale (1821) with capillary tubes of fused silica and of Elford (1922) with optically polished plates of quartz. Since the surface conductivity remains of the same order of magnitude with different concentrations of the solution, whereas the specific conductivity (volume) increases nearly a thousand-fold between 0.001 and 1.0 N, it follows that accurate determinations of surface conductivity may only be made with dilute solutions, the experimental error for stronger solutions mounting almost in proportion to the concentration. Hence the results for 0.001 N potassium chloride are the most significant. Thus in some of the cells the surface conductivity is quite half of the conductivity of the solution in the capillary.

TABLE XVI

SPECIFIC SURFACE CONDUCTIVITY IN THE NEIGHBORHOOD OF OPTICALLY POLISHED GLASS SURFACES IN THE PRESENCE OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE, EXPRESSED IN MHOS × 10^8 PER SQ. CM.

Concn., *N*	Dale fused silica	Elford polished quartz	No. of glass slit and table reference: No 1 III	No. 2 III, IV	No 4 VIII	No. 4 V	No 4 VI, VII	No. 5 X	No. 6 XI	No. 7 VII	No. 7 V, VI	No. 10 IX	Mean
0.1	..	....	3.0	(2.0)	..	...	...	6.0	..	13.0	...	...	(...)
.01	16.6	...	1.8	(3.8)	19.0	7.6	6.2	5.5	17.0	12.0	...	5.1	9.3
.002	..	5.6	6.1	(3.3)	..	5.9	2.8	...	..	6.3	...	...	5.3
.001	3.6	3.9	5.3	(2.4)	3.8	3.6	3.3	5.2	4.9	5.0	3.0	...	4.3

The results in Table XVI not only demonstrate the existence of surface conductivity but also yield approximate numerical values for the absolute specific surface conductances at optically polished glass surfaces. The surface conductances at smooth surfaces of fused silica or of optically polished quartz are the same as with polished glass. The surface conductivity of an insoluble film of fatty acid on water is of about the same magnitude.

Contrary to expectation on the basis of the dissociated double layer of Gouy, the surface conductivity seems to increase with increasing concentration of salt. Evidently the surface conductivity has a finite value even in the presence of 1.0 N salt, although it is less than 0.1% of the bulk conductivity even in the narrowest capillary spaces here used. Experiments on electroosmosis likewise show that, although fairly low concentrations of such salts as potassium chloride slow down the flow of liquid markedly, even large concentrations do not entirely stop it.

The negative ions which give the negative charge to the glass might be either OH^- or Cl^-, or even a mixture of the two.[18] Indeed it would be remarkable if there were not a small proportion of positive ions such as H^+ and K^+ also adsorbed on the glass. The corresponding free mobile ions in the solution would not be H^+ (or OH^-) because of the prolonged rinsing with further solution of potassium chloride, which would leave mostly K^+ (and for any positive ion adsorbed, a corresponding excess of Cl^-).

If the surface conductivity is entirely due to free mobile ions (K^+ and Cl^- whose mobility is in both cases 75 at 25°) then the specific surface conductivity, 4.3×10^{-8} mhos, equals 5.7×10^{-7} gram equivalents or 3.5×10^{14} actual ions. Now the distance between centers in a cubic face of potassium chloride crystal is 2.81×10^{-8} cm., when it follows that such a face comprises 12.7×10^{14} ions. Therefore, the surface conductivity in the presence of 0.001 N potassium chloride, if interpreted as free mobile ions, corresponds to one-third of the ions which could be accommodated in a monomolecular layer. That for higher concentrations approaches the value for a monomolecular layer.

One of us[19] has pointed out the erroneous voltages which necessarily

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[18] H. J. Weiland, THIS JOURNAL, 40, 131 (1918), found that the addition of ground quartz raised the conductivity of 0.001 *N* potassium chloride by 0.02% and that of conductivity water (1×10^{-6}) by 10 or more per cent. The ratio between the area of quartz surface and the volume in cubic centimeters is about 80. He interpreted his figures to the effect that 88×10^{-12} equivalents of potassium chloride were adsorbed per sq. cm. of quartz surface. Elford in similar experiments with bundles of fine fibers of fused silica likewise found that the conductivity of 0.001 *N* potassium chloride was raised by 0.1% and that of conductivity water (1.8×10^{-6}) by 69%. Weiland called the effect on water "pollution." We interpret it as adsorption of OH^-, creating an excess conductivity through liberation of H^+. With potassium chloride, if only Cl^- is adsorbed, the conductivity is to that extent diminished; if, as the other extreme, only OH^- were adsorbed, the conductivity would be greatly increased. The balance observed would indicate that about five times as much Cl^- as OH^- is adsorbed. Our interpretation is reinforced by Weiland's figures, which, according to his interpretation, show an adsorption equal to only a few per cent. of that required to explain the actual surface conductivity here found. Several observers have noted that electrokinetic phenomena are rather fluctuating or ill defined with solutions of potassium chloride and glass.

[19] J. W. McBain, *J. Phys. Chem.*, 28, 706 (1924). It is 56 volts for an interspace of 1×10^{-8} cm. between the two layers, and the same for 80×10^{-8} cm. if the di-

arise, from the formula for a condenser, if a complete monomolecular layer of ions all of one sign is compensated by an equal number of opposite sign. This might be reduced somewhat if the ions primarily adsorbed were not all of one sign, but the even more obvious alternative here is to ascribe some of the surface conductivity to mere concentration of the salt solution in the neighborhood of the surface. If this were the chief effect, the concentration of 0.001 N potassium chloride in the neighborhood of the glass surface would be raised to $^1/_2 \times 5.7$ N or $^1/_2 \times 0.57$ N, depending upon whether 10×10^{-8} or 100×10^{-8} cm. were taken as the effective range of molecular attraction. The concentration of hydrogen ions in equilibrium with a monomolecular layer of insoluble fatty acid appears to be about one-ninth of the total number of molecules in the oil film, no easy alternative being available. For comparison with the results of Table XVI it may be mentioned that 15.5×10^{-8} mhos would be the conductivity of free potassium ions taken equal in number to the atoms in a square centimeter of a surface of potassium chloride crystal.

To the many objections[19] revealing the fictitious nature of electrokinetic potential, ζ, may be added the assumption that the conductivity in the neighborhood of the surface is the same as the bulk conductivity, an assumption sufficiently disproved by the present work.

Another method of evading the fact that the surface conductivity corresponds to enough ions to cover quite one-third of a monomolecular layer is to assume that the mobility of a potassium ion in the neighborhood of the surface is different from that in the bulk of the solution. However, if the mobility is less, the concentration of ions must be more, and it is in proportion to the change in magnitude of the mobility that the number of ions deduced changes. It is very difficult to justify an *ad hoc* assumption that the actual mobility of the ions is much greater in the neighborhood of a solid surface of opposite charge. Adhesion tests in shear on such optically polished surfaces as are here studied show that the resistance encountered is of the order of one ton per square inch of polished surface,[20] negativing the idea of slip or facile flow.

One possibility remains, arising from the general formulations of Miss Laing[21] for movement in an electrical field, where it is shown that the movement with reference to the solvent is the same in electroösmosis as

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electric constant of water be taken as usual at 80. The suggestion made by several adherents of the theory of complete dissociation, that the dielectric constant of water in the neighborhood of ions is to be imagined as 6, raises the latter voltage to $80/6 \times 56 = 747$ volts, as, for example, between a solution and its glass container, provided, of course, that the layer is complete.

[20] J. W. McBain and W. B. Lee, *Proc. Roy. Soc. London*, **113A,** 606 (1926); *J. Soc. Chem. Ind.*, *46*, 321T (1927); *Ind. Eng. Chem.*, *19*, 1005 (1927); *J. Phys. Chem.*, **31,** 1674 (1927).

[21] M. E. Laing, *ibid.*, 28, 673 (1924).

in electrophoresis. If that is the case here and if the movement of solvent relative to the glass is about the same as the movement of the potassium ions through it, the total movement would about double the absolute velocity of the positive ions and would therefore halve the number deducible from the conductivity, giving only about $^1/_6$ of the number required to build a monomolecular layer. If the average distance of the mobile ions from the sessile charges on the glass is 80 X 10^{-8} cm., this would be equivalent to *a* condenser of about 9 volts: or: if the average separation of the mobile ions from the sessile ions is the same as the average distance between the ions throughout a normal solution of any salt such as potassium chloride, 10 × 10^{-8} cm., the voltage would be about one. However, if the mobile ions are not all of the same sign, which is almost inevitable, the voltage is very greatly reduced, although the Laing effect would be less than that just indicated for the extreme case. This conception assumes that the sessile ions are both positive and negative, the majority being negative.

Finally, it has been common knowledge for a generation or more that a glass surface, once exposed to an aqueous solution, is partially leached out so that it is superficially porous, and the less well-known facts may be recalled that the very best optically polished surfaces are full of infinitesimal cracks; therefore the actual surface of glass is much greater than appears from macroscopic examination. With surfaces such as here used, possibly true to 2–300 Å., these effects do not invalidate or possibly do not even appreciably change our results, although they are in the direction emphasizing the incompleteness of any layer of charges upon the glass, fused silica or polished quartz.

In our experiments with ordinary pyrex tubing[8] the value of the specific surface conductivity for 0.001 potassium chloride is 13 X 10^{-8} mhos as compared with the 4.3 × 10^{-8} mhos here found for optically polished glass.

Surface conductivity exists and has to be taken into account in any discussion of the electrical behavior or sorption equilibria of capillary spaces, or finely divided matter such as colloids or organisms containing an ionizing solvent.

Summary

For the first time absolute measurements of specific surface conductivity have been made. For aqueous 0.001 N potassium chloride at 25° the extra conductivity in the neighborhood of optically polished glass, fused silica and optically polished quartz amounts to a specific surface conductivity of 4.3 X 10^{-8} mhos. Thus in capillary spaces of less than 0.01 mm. half the conductivity may be surface conductivity, ascribable to free mobile ions corresponding to sessile ions of opposite charge upon the solid interface, which are probably not all of negative sign. These mobile

ions are not sufficiently numerous to form more than about one-eighth of a monomolecular layer. This is of the same order as that found in our measurements of specific surface conductivity of an insoluble fatty acid on conductivity water.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. VI. ETHYL IODIDE, ETHANOL, NORMAL-BUTANOL AND NORMAL-OCTANOL

BY C. P. SMYTH AND W. N. STOOPS

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The extreme complexity of the dielectric behavior of the alcohols as observed by various investigators over a limited range of temperature or of concentration, together with the importance of the electric moments of this group of substances, has made it desirable to measure several alcohols from the pure liquid to the most dilute solutions in non-polar solvents over the entire range of temperature within which they are liquid. The methods of measurement and calculation used in the present work have been described in the first two papers of the series on dielectric polarization.[1] In these earlier measurements, benzene and hexane were employed as non-polar solvents, the latter being particularly useful because of the wide range of temperature within which it is liquid. Since pure normal heptane can now be obtained much more readily than hexane of a comparable purity and, at the same time, is liquid over a wider temperature range, it has replaced hexane in the present determinations. Although it had been found that none of the isomers of heptane had detectable electric moments and the similarity of heptane to hexane[2] indicated that it would give identical results as a non-polar solvent, three solutions of ethyl bromide in heptane were measured for comparison with those in hexane previously studied. The results showed the expected agreement and are, therefore, omitted from this paper. However, measurements upon the similar substance, ethyl iodide, are reported and ethyl alcohol has been studied in both hexane and heptane with results that show similar behavior in the two solvents.

Method of Measurement

The densities were determined with the same type of pycnometer used in the earlier work and the dielectric constants were measured with the

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[1] Smyth, Morgan and Boyce, THIS JOURNAL, 50,1536 (1928); Smyth and Morgan, *ibid.*, 50, 1547 (1928).

[2] Smyth and Stoops, *ibid.*, 50, 1883 (1928).

capacity bridge previously described, a frequency of 5 X 10^5 cycles, corresponding to a wave length of 600 meters, being used as before. The constancy of the wave length was checked by means of a wave meter, and the platinum resistance thermometer was calibrated at −95.1°, the freezing point of toluene, at 0°, and at 100° and checked occasionally at the ice point to make sure that there was no change. In addition to the condenser cell with platinum cylinders used in the earlier work, a cell, similar in form but consisting of three concentric brass cylinders, heavily gold plated, was employed. This differed further from the platinum cell in that the cylinders had separate leads and could thus be connected together in different combinations having capacities of 66, 40, 27 and $17\mu\mu$f., as compared to the $200\mu\mu$f. of the platinum cell, the outer cylinder always being grounded as in the latter.

The errors involved are not very different from those in the earlier work. The probable error in the densities measured at low temperatures was 0.07% and in those above 0° not more than 0.03%. The dielectric constants of mixtures whose maximum value did not exceed five were measured in the platinum cell by direct substitution on the precision condenser. The probable error here was 0.2%, although the error within a given series of measurements was less. For other mixtures, measured either with the platinum cell in series with another variable air condenser or with the gold-plated cell, the accuracy was less, the probable error being 0.5%. Again the accuracy within a given series of measurements was greater. When considerable resistance was required in the balancing arm to compensate for conductance or absorption in the cell, the dielectric constants are probably not accurate to more than 2%. These large resistances were necessary only in the case of the pure alcohols and their most concentrated solutions at low temperatures. The effect of the resistance was to cause the apparent values of the dielectric constants to be too large. The change in concentration due to evaporation of the more volatile component at the highest temperatures was troublesome in the dilute mixtures, but error from this source was corrected by comparison of measurements made at room temperature before and after the high temperature determinations.

Preparation of Materials

Heptane.—Pure normal heptane was obtained from the Ethyl Gasoline Corporation. A portion of it was washed with sulfuric acid, then with dilute sodium carbonate solution and with water. It was dried over calcium chloride, and finally distilled over sodium. As the boiling point, refractive index and dielectric constant were not appreciably different after this treatment, the heptane was normally used without purification.

Ethyl **Iodide.**—C. P. ethyl iodide was washed repeatedly with water, dried over fused calcium chloride and fractionally distilled; b. p. 72 4–72.5" at 773.7 mm.

Benzene.—Merck's C. P. benzene was washed three times with sulfuric acid, then with dilute sodium carbonate solution and with water, dried over calcium oxide and twice fractionally crystallized. It was then dried over sodium and fractionally distilled; b. p. 80.1°; n_D^{20} 1.50139.

Cyclohexane.—Eastman's purified grade cyclohexane was fractionally crystallized. The fractions melting at 6.2 and 6.0° were mixed, dried over sodium and fractionally distilled; b. p. 80.90–80.95°.

Ethyl Alcohol.—Ninety-five per cent. ethyl alcohol was refluxed over freshly ignited calcium oxide for twenty-four hours, the lime being changed once during this time, and fractionally distilled; b. p. 78.4°; n_D^{20} 1.36139.

Butyl Alcohol.—Normal butyl alcohol from the Commercial Solvents Corporation, b. p. 114–117°, was refluxed over freshly ignited lime and fractionally distilled; b. p. 117.2–117.4"; n_D^{20} 1.39922. A sample prepared by Dr. H. B. Glass at Johns Hopkins University was used in some of the work; b. p. 117.2–117.3°; n_D^{20} 1.39920.

Octyl Alcohol.—n-Octyl alcohol was obtained from the Eastman Kodak Company and fractionated by Dr. H. B. Glass and Dr. G. B. Malone working with Professor E. Emmet Reid of Johns Hopkins University.

Experimental Results

The densities, which showed only a small departure from a linear dependence upon temperature, were determined at 20–25° intervals and the dielectric constants at approximately 15° intervals, except when the temperature variation of the latter was so great as to necessitate 5–10' intervals. The densities, *d*, and dielectric constants, ϵ, in Table II were obtained at 10° intervals by graphical interpolation and the polarizations, P_2, of the polar components were calculated from them by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{c_1M_1 + c_2M_2}{d} \text{ and}$$

$$P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights

TABLE I

DIELECTRIC CONSTANTS AND COMPENSATING RESISTANCES FOR ETHANOL AND n-BUTANOL

t, °C.	ϵ	R	t, °C.	ϵ	R	t, °C.	ϵ	R
	C_2H_5OH		41.7	20.9	14.4	−67.4	30.8	29.7
−110.4	56.6	34.2	55.4	18.8	18.7	−62.3	30.2	20.3
−104.7	54.3	20.5	73.5	17.5	25.0	−58.3	29.5	15.5
−93.0	50.3	9.5		n-C_4H_9OH		−49.7	27.8	8.5
−88.8	48.9	7.5	−96.9	2.60	1.5	−39.9	26.2	4.9
−75.9	44.7	4.2	−92.9	2.79	2.3	−30.8	24.8	3.3
−67.1	42.0	3.3	−91.3	3.02	4.0	−19.9	22.9	2.5
−54.2	38.5	3.0	−88.7	20.3	85.0	−7.3	21.0	2.4
−43.4	35.7	3.1	−86.3	24.0	90.0	5.5	19.2	2.8
−31.6	33.0	3.6	−84.6	26.2	88.2	17.2	17.7	3.6
−19.5	30.5	4.3	−80.8	29.5	76.7	29.4	16.2	4.6
−7.5	28.3	5.2	−77.6	30 9	63.4	44.0	14.4	5.9
4.7	26.2	6.6	−76.4	31.1	58.4	56.8	13.1	7.3
17.0	24.2	8.4	−74.0	31.3	49.0	71.7	11.6	9.2
29.3	22.5	11.4	−71.7	31.4	41.4			

and polarizations of the individual components. The values of P_2 for ethyl iodide are omitted as they vary regularly with concentration. In Table I the dielectric constant values for pure ethyl alcohol and butyl alcohol are given, together with the compensating series resistances, R, in ohms which had to be used to balance out the effects of conductance or absorption in the measuring cell. This resistance gives an indication of the magnitude of the conductance and of the absorption of the liquid for a wave length of 600 meters.

TABLE II

INTERPOLATED VALUES OF DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AND POLARIZATIONS OF POLAR COMPONENTS

Heptane–Ethyl Iodide

Mole fr., C_2H_5I =	0.0328	0.0365	0.0843	0.1889	0.4130	0.6155	0.8035	1.000
t, °C.								
−100	2.258	2.266	2.522	3.053	4.541	6.52		
−90	2.234	2.244	2.484	2.991	4.408	6.25	8.96	12.27
−80	2.211	2.220	2.447	2.932	4.277	6.02	8.55	11.64
−70	2.188	2.198	2.412	2.875	4.158	5.79	8.19	11.11
−60	2.168	2.177	2376	2.820	4.040	5.59	7.87	10.60
−50	2.147	2.157	2.346	2.766	3.927	5.405	7.58	10.16
−40	2.128	2.137	2.316	2.719	3.824	5.235	7.30	9.74
−30	2.109	2.117	2.287	2.673	3.723	5.075	7.03	9.36
−20	2.089	2.098	2.257	2.628	3.630	4.920	6.78	9.01
−10	2.070	2.078	2.230	2.584	3.539	4.774	6.54	8.67
0	2.051	2.059	2.203	2.541	3.456	4.630	6.31	8.38
10	2.032	2.039	2.177	2.501	3.372	4.493	6.09	8.10
20	2.014	2.022	2.154	2.462	3.296	4.360	5.88	7.82
30	1.995	2.003	2.134	2.422	3.220	4.240	5.66	7.56
40	1.977	1.984	2.113	2.383	3.149	4.122	5.46	7.29
50	1.959	1.964	2.093	2.349	3.078	4.017	5.27	7.03
60	1.940	1.944	2.074	2.314	3.010	3.909	5.08	6.80
70	1.920	1.922	2.057	2.280	2.940	3.809	4.89	6.59
t, °C.					d			
−100	0.8075	0.8106	0.8495	0.9382	1.1734	1.4413		
−90	.7990	.8018	.8407	.9287	1.1615	1.4265	1.7408	2.1777
−80	.7906	.7936	.8317	.9188	1.1491	1.4117	1.7226	2.1548
−70	.7822	.7852	,8228	.9089	1.1370	1.3966	1.7044	2.1321
−60	.7737	.7766	.8138	.8993	1.1248	1.3820	1.6862	2.1094
−50	.7652	.7682	.8049	.8898	1.1126	1.3671	1.6682	2.0867
−40	,7570	.7596	.7960	.8802	1.1003	1.3523	1.6503	2.0640
−30	.7484	.7514	.7872	.8705	1.0882	1.3377	1.6324	2.0411
−20	.7398	.7430	.7781	.8607	1.0761	1.3228	1.6140	2.0187
−10	.7313	.7342	.7692	.8510	1.0637	1.3078	1.5961	1.9967
0	.7231	.7252	.7604	.8411	1.0515	1.2927	1.5778	1.9740
10	.7142	.7168	.7513	.8315	1.0394	1.2775	1.5593	1.9514
20	.7058	.7082	.7422	.8215	1.0271	1.2622	1.5410	1.9288
30	.6971	.6995	.7333	.8112	1.0140	1.2471	1.5226	1.9062
40	.6881	.6905	.7238	.8005	1.0010	1.2315	1.5038	1.8831

TABLE II (*Continued*)

Mole fr., C_2H_5I =	0.0328	0.0365	0.0843	0.1889	0.4130	0 6155	0.8035	1.000
t, °C.	*d*							
50	0.6791	0.6815	0.7144	0.7897	0.9879	1.2155	1.4844	1.8600
60	.6702	.6726	,7047	.7789	.9747	1.1998	1.4648	1.8368
70	.6609	.6635	,6950	.7684	.9610	1.1836	1.4460	1.8133

Hexane–Ethyl Alcohol

Mole fr., C_2H_5OH =	0.0153	0.0578	0.0962	0.2076	0.0153	0.0578	0.0962	0.2076
t, °C.					d			
−90	2.093	2.160	2.259	3.418	0.7820	0.7842	0.7844	0.7945
−80	2.077	2 144	2 248	3.360	.7742	.7755	.7763	.7857
−70	2.060	2 129	2.232	3.295	.7660	.7670	.7682	.7771
−60	2.045	2.114	2.214	3.225	.7574	.7582	.7599	.7703
−50	2.030	2.098	2.197	3.150	.7483	.7495	.7525	.7611
−40	2.016	2 083	2.179	3.075	.7397	.7408	.7430	.7518
−30	2.002	2 068	3.162	2.996	.7310	.7321	.7344	.7423
−20	1.989	2.054	2.145	2.913	.7220	.7235	.7256	.7330
−10	1.976	2.040	2.128	2.830	.7130	.7148	.7169	.7240
0	1.964	2.026	2.111	2.755	.7040	.7060	.7076	.7143
10	1.952	2.014	2.096	2.687	.6950	.6965	.6983	.7051
20	1.940	2.002	2.082	2.622	.6859	.6874	.6890	.6960
30	1.928	1.990	2.069	2.563	.6766	.6782	.6797	.6864
40	1.914	1.978	2.054	2.507	.6671	.6690	.6700	.6770
50	1.898	1.968	2.039	2.453	.6577	.6589	.6601	.6670
60	1.882	1.958	2.025	2.403	.6476	.6480	.6501	.6571

t, °C.	$P_2(C_2H_5OH)$			
−90	33.1	40.4	48.4	99.3
−80	31.1	40.7	49.9	98.7
−70	28.5	41.9	50.2	97.8
−60	30.5	42.0	50.3	95.8
−50	31.8	43.1	50.4	94.4
−40	35.7	43.8	50.8	92.5
−30	35.1	43.6	50.8	90.3
−20	37.7	44.4	51.1	87.4
−10	42.3	45.5	51.6	84.5
0	46.2	46.7	51.9	81.9
10	50.8	48.5	52.6	79.6
20	58.7	50.8	53.8	77.0
30	64.5	52.5	55.4	75.1
40	70.4	55.4	56.6	73.3
50	77.5	60.2	58.6	71.7
60	83.4	66.2	60.9	70.4

Heptane–Ethyl Alcohol

Mole fr., C_2H_5OH =	0.0256	0.4252	0.6142	0.8300	0.9260	1.000
t, °C.						
−110						56.4
−100	2.129					52.9

TABLE II (*Continued*)

Mole fr., C_2H_5OH =	0.0256	0.4252	0.6142	0.8300	0.9260	1.000
t, °C.						
−90	2.113				40.8	49.3
−80	2.099			29.8	38.1	46.1
−70	2 084			28 0	35.6	43.0
−60	2 069			26 3	33.2	40.1
−50	2.053			24.7	31.0	37.4
−40	2 040			23.1	29.0	35.0
−30	2.027	5.80	11.02	21 7	27.2	32.7
−20	2.015	5.55	10.40	20 3	25.5	30.7
−10	2.003	5.31	9.96	19 0	24 0	28.7
0	1.991	5.06	9.43	17.8	22.5	27.0
10	1.980	4 82	8.92	16 6	21.1	25.3
20	1.968	4.59	8 40	15 5	19.8	23.8
30	1.956	4.36	7.87	14.5	18.6	22.4
40	1.944	4.14	7.39	13 6	17.4	21.0
50	1.931	3 95	6 92	12 7	16.3	19.8
60	1.915	3.76	6.48	11.8	15.2	18.7
70	1.900	3.59	6.05	11 0	14.2	17.6
t, °C.			*d*			
−110						0.9031
−100	0.7830					.8941
−90	.7749				0.8649	.8852
−80	.7669			0.8369	.8562	.8762
−70	.7586			.8281	.8476	.8674
−60	.7503			.8193	.8390	.8586
−50	.7422			.8108	.8303	.8498
−40	.7340			.8022	.8216	.8412
−30	.7259	0.7487	0.7657	.7938	.8132	.8327
−20	.7177	.7400	.7572	.7851	.8048	.8242
−10	.7092	.7317	.7488	.7766	.7962	.8158
0	.7010	.7232	.7401	.7678	.7876	.8073
10	.6927	.7146	.7314	.7590	.7790	.7988
20	.6843	.7058	.7226	.7500	.7702	.7901
30	.6760	.6968	.7139	.7411	.7617	.7816
40	.6671	.6876	.7048	.7322	.7528	.7727
50	.6582	.6782	.6953	.7233	.7436	.7638
60	.6494	.6688	.6858	.7143	.7344	.7547
70	.6404	.6592	.6760	.7053	.7251	.7456
t, °C.			$P_2(C_2H_5OH)$			
−110						48.5
−100	44.4					48.7
−90	43.3				55.4	49.0
−80	43.3			65.0	55.7	49.3
−70	42.9			65.3	55.9	49.6
−60	42.6			65.6	56.2	49.8
−50	41.1			65.8	56.4	50.1
−40	41.8			66.0	56.7	50.3

TABLE II (*Continued*)

Mole fr., C_2H_5OH =	0.0256	0.4252	0.6142	0.8300	0.9260	1.000
t, °C.	$P_2(C_2H_5OH)$					
−30	42.7	102.6	87.8	66.2	56.9	50.5
−20	44.7	101.2	87.7	66.3	57.1	50.7
−10	47.8	99.8	87.3	66.4	57.3	50.9
0	49.9	97.6	86.8	66.5	57.5	51.1
10	53.0	95.4	86.2	66.4	57.6	51.3
20	55.9	93.2	85.5	66.5	57.8	51.5
30	58.0	90.7	84.4	66.4	57.9	51.7
40	61.7	88.0	83.3	66.3	57.9	51.8
50	64.2	85.5	82.2	66.1	58.0	52.0
60	63.4	82.9	80.8	65.8	58.0	52.2
70	63.8	80.5	79.2	65.3	58.0	52.3

Heptane–*n*-Butyl Alcohol

Mole fr., C_4H_9OH =	0.0312	0.0525	0.0805	0.1042	0.1383	0.2655	0.4451	0.6152	0.8042	1.000
t, °C.										
−90	2.113	2.131	2.196	2.223		4.790	9.27		16.3	
−80	2.098	2.118	2.168	2.208	2.360	4.703	10.32	16.85	24.0	30.0
−70	2.082	2.105	2.148	2.194	2.333	4.502	10.31	16.20	24.4	31.3
−60	2.068	2.092	2.134	2.179	2.308	4.177	9.61	15.40	23.0	29.8
−50	2.052	2.080	2.122	2.164	2.285	3.889	8.89	14.44	21.6	27.9
−40	2.041	2.066	2.109	2.149	2.263	3.628	8.18	13.40	20.0	26.2
−30	2.028	2.054	2.096	2.136	2.241	3.401	7.48	12.40	18.6	24.6
−20	2.016	2.042	2.084	2.123	2.221	3.200	6.80	11.44	17.3	22.9
−10	2.004	2.032	2.073	2.111	2.203	3.040	6.13	10.49	16.0	21.4
0	1.993	2.021	2.063	2.100	2.186	2.910	5.55	9.57	14.9	20.0
10	1.982	2.011	2.053	2.088	2.167	2.798	5.16	8.78	13.8	18 6
20	1.972	2.001	2.044	2.077	2.153	2.696	4.82	8.00	12.6	17.4
30	1.961	1.991	2.034	2.068	2.141	2.608	4.48	7.30	11.6	16.1
40	1.950	1.980	2.024	2.058	2.132	2.547	4.19	6.64	10.6	14.9
50	1.936	1.969	2.013	2.046	2.118	2.500	3.92	6.07	9.71	13.8
60	1.921	1.955	2.001	2.034	2.105	2.454	3.70	5.54	8.72	12.8
70	1.907	1.939	1.986	2.019	2.089	2.416	3.53	5.11	8.01	11.8
80	1.890	1.921	1.968	2.003	2.070	2.384	3.39	4.80	7.30	10.8
90	1.872	1.902	1.949	1.985	2.042	2.348	3.26	4.46	6.69	9.9
t, °C.						*d*				
−90	0.7760	0.7775	0.7798	0.7812		0.7948	0.8134	0.8261	0 8604	
−80	.7679	.7692	.7718	.7732	0.7762	.7868	.8054	.8182	,8526	0.8872
−70	.7598	.7612	.7636	.7651	,7680	.7789	.7974	.8101	,8448	.8793
−60	.7514	.7530	.7552	.7570	.7600	.7709	.7895	.8022	.8369	.8713
−50	.7432	.7450	.7473	.7489	.7518	.7630	.7815	.7942	.8289	.8634
−40	.7352	.7369	.7391	.7409	.7437	.7552	.7736	.7862	.8211	.8556
−30	.7272	.7289	.7311	.7329	.7355	.7470	.7657	.7782	.8132	.8479
−20	.7192	.7208	.7231	.7249	.7267	.7388	.7577	.7701	.8053	.8402
−10	.7108	.7126	.7148	.7164	.7184	.7305	.7494	.7621	.7974	.8328
0	.7024	.7040	.7062	.7081	.7101	.7222	.7414	.7540	,7897	.8250
10	.6940	.6958	.6980	.6997	.7017	.7139	.7331	.7458	.7820	.8173

TABLE II *(Continued)*

Mole fr., C_4H_9OH =	0.0312	0.0525	0.0805	0.1042	0.1383	0.2655	0.4451	0.6152	0.8042	1.000
t, °C.	*d*									
20	0.6854	0.6872	0.6895	0.6911	0.6936	0.7053	0.7247	0.7376	0.7737	0.8098
30	.6769	.6788	.6810	.6826	.6855	.6970	.7160	.7289	.7657	.8022
40	.6681	.6700	.6722	.6739	.6767	.6882	.7072	.7201	.7574	.7945
50	.6591	.6610	.6631	.6650	.6682	.6796	.6987	.7115	.7491	.7867
60	.6502	.6520	.6539	.6559	.6597	.6709	.6898	.7022	.7410	.7787
70	.6412	.6428	.6447	.6467	.6512	.6616	.6803	.6930	.7320	.7703
80	.6320	.6333	.6350	.6372	.6424	.6525	.6710	.6839	.7231	.7616
90	.6239	.6240	.6257		.6334	.6431	.6616		.7140	.7527
t, °C.	$P_2(C_4H_9OH)$									
−90	46.7	44.3	53.7	52.2		151.8	136.8		87.4	
−80	45.2	45.0	50.3	52.2	66.8	151.6	144.1	117.8	93.9	75.7
−70	43.9	45.8	48.1	52.4	65.6	147.8	145.8	119.1	94.9	76.7
−60	45.6	46.5	49.6	52.9	64.7	139.2	144.0	119.2	95.2	77.0
−50	44.0	47.7	50.4	53.3	63.9	130.6	141.5	117.8	95.4	77.2
−40	46.3	48.9	51.2	53.6	63.6	121.8	138.4	117.1	95.4	77.4
−30	47.3	48.8	51.9	54.2	62.8	113.5	134.7	116.1	95.2	77.5
−20	48.3	50.5	52.6	54.9	62.7	105.6	130.0	114.9	94.9	77.6
−10	49.0	52.3	54.0	56.8	62.8	98.9	124.6	113.3	94.6	77.6
0	51.2	53.8	55.8	56.9	62.9	93.4	118.7	111.3	94.2	77.6
10	55.4	56.3	57.4	57.9	62.8	88.5	114.4	109.3	93.6	77.6
20	59.3	59.2	60.0	50.2	63.4	84.0	111.6	106.7	92.8	77.3
30	62.9	61.4	61.9	60.4	64.3	79.8	106.0	103.9	91.9	77.0
40	66.4	64.1	64.0	62.1	66.0	77.4	101.6	100.7	90.8	76.6
50	68.1	66.6	66.3	63.7	67.0	76.0	97.1	97.6	89.3	76.3
60	68.4	68.0	68.3	65.6	67.9	74.5	93.1	93.9	87.3	76.0
70	69.7	68.5	69.5	66.9	68.5	73.5	90.3	90.8	85.8	75.4
80	70.7	69.1	70.1	68.4	68.6	73.5	87.9	88.5	83.9	74.5
90	67.8	68.9	70.2		67.0	73.0	85.9	85.3	81.8	73.7

Cyclohexane–*n*-Butyl Alcohol

Mole fr., C_4H_9OH =	0	0.0391	0.1102	0.2002	0	0.0391	0.1102	0.2002
t, °C.					*d*			
10	2.041	2.108	2.272	2.743	0.7877	0.7878	0.7889	0.7905
20	2.027	2.099	2.260	2.674	.7784	.7783	.7795	.7813
30	2.013	2.088	2.248	2.623	.7690	.7690	.7701	.7721
40	1.998	2.076	2.236	2.579	.7594	.7593	.7605	.7625
50	1.981	2.061	2.224	2.537	.7498	.7494	.7508	.7528
60	1.963	2.045	2.210	2.497	.7398	.7387	.7407	.7428
70	1.944	2.028	2.192	2.458	.7299	.7282	.7308	.7326

t, °C.	$P_1(C_6H_{12})$	$P_2(C_4H_9OH)$		
10	27.50	57.2	62.3	80.8
20	27.55	60.5	63.3	77.9
30	27.61	62.4	64.4	76.2
40	27.65	64.7	65.6	74.9
50	27.64	67.0	67.4	74.1
60	27.62	70.1	69.3	73.4
70	27.58	72.7	70.3	72.9

TABLE II (Continued)

Benzene–n-Butyl Alcohol

Mole fr., C_4H_9OH =	0	0.0211	0.0578	0.0798	0.1117	0.2525	0.4899	0.7385
t, °C.	ε							
10	2.315	2.400	2.548	2.655	2.835	4.066	8.29	14.03
20	2.294	2.378	2.526	2.631	2.797	3.899	7.58	12.84
30	2.274	2.354	2.502	2.600	2.756	3.747	6.94	11.72
40	2.253	2.330	2.473	2.565	2.713	3.604	6.37	10.68
50	2.231	2.304	2.438	2.525	2.665	3.472	5.96	9.74
60	2.209	2.274	2.401	2.480	2.612	3.350	5.43	8.91
70	2.186	2.243	2.358	2.435	2.555	3.238	5.03	8.11
t, °C.	*d*							
10	0.8899	0.8875	0.8843	0.8824	0.8801	0.8693	0.8523	0.8354
20	.8791	.8768	.8738	.8719	.8695	.8591	.8430	.8269
30	.8682	.8661	.8632	.8615	.8591	.8489	.8334	.8182
40	.8574	.8553	.8528	.8512	.8489	.8388	.8240	.8095
50	.8466	.8447	.8421	.8403	.8378	.8284	.8142	.8007
60	.8358	.8338	.8311	.8296	.8270	.8180	.8048	.7917
70	.8250	.8231	.8203	.8188	.8162	.8076	.7948	.7826
t, °C.	$P_1(C_6H_6)$	$P_2(C_4H_9OH)$						
10	26.73	84.6	82.4	84.3	86.9	98.3	101.3	89.5
20	26.75	85.2	83.4	85.0	86.5	95.3	98.7	88.7
30	26.80	83.8	83.7	84.4	85.6	92.6	96.0	87.7
40	26.82	82.9	82.7	83.1	84.4	89.6	93.0	86.4
50	26.82	81.0	80.8	81.3	82.7	87.0	91.0	85.0
60	26.82	76.7	78.5	78.5	80.3	84.4	87.1	83.6
70	26.80	71.9	74.5	75.9	77.5	82.0	84.1	81.8

Heptane–n-Octyl Alcohol

Mole fr., $C_8H_{17}OH$ =	0.0447	0.0671	0.1260	0.2347	0.4374	0.7360	1.000
t, °C.	ε						
−30	2.046	2.070	2.162	2.489	4.928	11.22	
−20	2.033	2.059	2.152	2.457	4.456	10.21	
−10	2.021	2.049	2.141	2.426	4.045	9.25	13.31
0	2.010	2.039	2.131	2.399	3.770	8.36	12.26
10	2.000	2.029	2.122	2.376	3.554	7.52	11.26
20	1.991	2.020	2.114	2.357	3.384	6.78	10.34
30	1.981	2.012	2.107	2.341	3.233	6.14	9.45
40	1.971	2.004	2.100	2.326	3.130	5.60	8.62
50	1.960	1.994	2.091	2.311	3.030	5.14	7.84
60	1.948	1.982	2.082	2.295	2.943	4.75	7.09
t, °C.	*d*						
−30	0.7318	0.7364	0.7438	0.7591	0.7881	0.8278	
−20	.7236	.7280	.7358	.7512	.7805	.8202	
−10	.7151	.7194	.7277	.7432	.7730	.8131	0.8461
0	.7068	.7109	.7193	.7351	.7650	.8058	.8391
10	.6987	.7023	.7111	.7272	.7573	.7985	.8322
20	.6904	.6940	.7028	.7192	.7498	.7912	.8253

Table II *(Concluded)*

Mole fr., $C_8H_{17}OH$ =	0.0447	0.0671	0.1260	0.2347	0.4374	0.7360	1.000
t, °C.				d			
30	0.6820	0.6853	0.6943	0 7113	0 7418	0.7838	0.8186
40	.6738	,6766	.6857	.7031	.7338	.7763	.8115
50	.6647	.6679	.6770	.6945	.7258	.7690	.8042
60	,6557	.6591	.6688	.6858	.7176	.7615	.7970
t, °C.				$P_2(C_8H_{17}OH)$			
−30	65.1	64.1	70.4	87.1	141.8	142.7	
−20	65.6	65.5	71.5	86.2	135.4	140.3	
−10	67.7	67.8	72.5	85.2	124.4	137.3	123.7
0	69.8	70.1	73.9	84.7	118.0	134.0	122.5
10	72.2	72.1	75.4	84.5	112.8	130.1	121.0
20	75.9	74.7	77.4	84.8	108.3	125.8	119.3
30	78.5	77.8	79.5	85.1	104.3	121.3	117.3
40	81.2	81.1	81.7	85.7	101.8	117.1	115.1
50	84.7	83.7	83.7	86.6	99.7	113.1	112.5
60	87.4	85.5	85.4	87.2	97.1	108.8	109.4

Benzene-n-Octyl Alcohol

Mole fr., $C_8H_{17}OH$ =	0.0280	0.0406	0.0492	0.0666	0.0860	0.0280	0.0406	0.0492	0.0666	0.0860
t, °C.			ϵ					d		
10	2.420	2.464	2.490	2.556	2.619	0.8864	0.8852	0.8840	0.8822	0.8802
20	2.398	2.442	2.468	2.535	2.599	.8759	.8748	.8737	.8720	.8699
30	2.374	2.418	2.444	2.510	2.576	.8654	.8643	.8634	.8618	.8597
40	2.348	2.391	2.417	2.482	2.549	.8549	.8539	.8531	.8514	.8494
50	2.321	2.361	2.387	2.450	2.516	.8443	.8433	.8426	.8409	.8391
60	2.292	2.331	2.355	2.414	2.479	.8334	.8326	.8317	.8301	.8286
70	2.263	2.300	2.323	2.376	2.438	.8226	.8219	.8210	.8195	.8182
t, °C.			$P_2(C_8H_{17}OH)$							
10	101.3	99.9	98.5	99.2	98.0					
20	101.4	100.4	98.9	100.1	99.2					
30	100.7	100.1	98.9	100.1	99.7					
40	98.6	98.7	97.7	99.6	99.6					
50	97.2	96.9	96.5	98.4	98.9					
60	94.7	95.0	94.7	96.5	97.4					
70	92.5	93.1	92.9	94.1	95.1					

Discussion of Results

In Table I the high compensating resistance for ethyl alcohol (freezing point −117.3') at low temperatures shows a considerable absorption although the dielectric constant has not begun to fall off even at −110.4'. For butyl alcohol, with its larger molecules, the absorption is noticeable at higher temperatures and the dielectric constant begins to fall off nearly 20° above the freezing point, −89.8°. On solidification the dielectric constant shows a tremendous decrease as the dipole contribution drops out and the absorption becomes negligible. The measurements on the heptane solutions of ethyl alcohol do not extend down to temperatures at which absorption is considerable, but the concentrated butyl alcohol solutions show an increasing absorption at low temperature and a decrease in the dielectric constant as −90° is approached. The effect is negligible in the concentrations measured below mole fraction 0.4451 of butyl alcohol. *n*-Octyl alcohol (freezing point −16.3°) was not measured at temperatures low enough to cause strong absorption, but the slight absorption observed in the pure alcohol diminished in the 0.7360 solution and was negligible in the 0.4374 solution at the same temperatures.

With rising temperature the compensating resistance decreases as the absorption decreases, then passes through a minimum and increases up to the highest temperatures measured, presumably because of electrolytic conductance which increases with rising temperature. The increase is not apparent in n-octyl, is considerable in butyl, large in ethyl and so large in methyl alcohol that the apparatus is inadequate for the measurements at higher temperatures. The minimum occurs at a lower temperature, the smaller the alcohol molecule. In the heptane solutions the effect decreases with decreasing concentration and is not evident in the concentrations measured below $c_2 = 0.6$.

When P_{12} at different temperatures is plotted against c_2, the mole fraction of ethyl iodide in the heptane-ethyl iodide mixtures, the curves obtained resemble those for ethyl bromide, passing through a maximum, which, however, is less pronounced than in the ethyl bromide curves. The P_2–c_2 curves also resemble those for ethyl bromide but possess a slightly smaller curvature. The polarization of the pure substance decreases slightly with rising temperature instead of increasing as does that of ethyl bromide. These facts indicate that the effect of orientation is less in ethyl iodide than in ethyl bromide, as would be expected from the slightly smaller electric moment, 1.66 X 10^{-18}, as compared to 1.86 X 10^{-18}, and the screening effect of the iodine atom, which should be greater than that of the bromine. When the P_2–c_2 curves are extrapolated to $c_2 = 0$, the values of P obtained give a straight line when plotted against $1/T$, as required by the Debye equation: $P = a + b/T$. The values of the constants a and b are obtained graphically from the values of P, in Table III and in order to show the linearity of the variation of P, with $1/T$, the values of $(P, - a)\ T = b$ are shown. There is evidently no departure from the linearity demanded by theory, the maximum deviation from the value b = 17,000 being less than 1%. The electric moment μ is calculated from b; the value of P_E, the electronic contribution to the polarization, is obtained by extrapolation to infinite wave length of the molar refraction for visible light, and the somewhat doubtful atomic contribution is obtained as $P_A = a - P_E$. The dipole contribution P is, of course, $P_\infty - a$. The value of the electric moment, 1.66 X

10^{-18}, agrees well with that obtained by Williams, 1.7×10^{-18}, from measurements at one temperature, and with the value 1.62×10^{-18} of Mahanti and Sen Gupta from measurements on the vapor.[3]

Table III

Polarization Contributions of Ethyl Iodide

T, °A.	P,	$(P_\infty - a)T$	T, °A.	P_∞	$(P_\infty - a)T$	T, °A	P_∞	$(P_\infty - a)T$
173	134.7	17150	233	108.9	17080	293	93.7	17020
183	128.3	16920	243	106.0	17100	303	91.9	17050
193	123.3	16930	253	102.6	16950	313	89.6	16900
203	119.6	17050	263	99.7	16850	323	88.1	16950
213	116.1	17150	273	97.5	16900	333	86.6	16970
223	112.6	17160	283	95.8	17040	343	85.0	16950

$a = 35.6$; $b = 17000$; $P_E = 23.3$; $P_a = 12.3$; $\mu = 1.66 \times 10^{-18}$.

An attempt to apply the Debye equation to solutions of ethyl alcohol in heptane meets with serious difficulties. The values of P_{12} and P_2 for dilute alcohol solutions increase with rising temperature instead of decreasing as the theory requires (Figs. 1 and 2). In these and the subsequent diagrams, one circle sometimes represents several almost coincident points on different curves. At slightly higher concentrations (c_2 = 0.12–0.20) of alcohol the P_{12}–c_2 and the P_2–c_2 curves at different temperatures intersect, the polarization becoming practically independent of tempera-

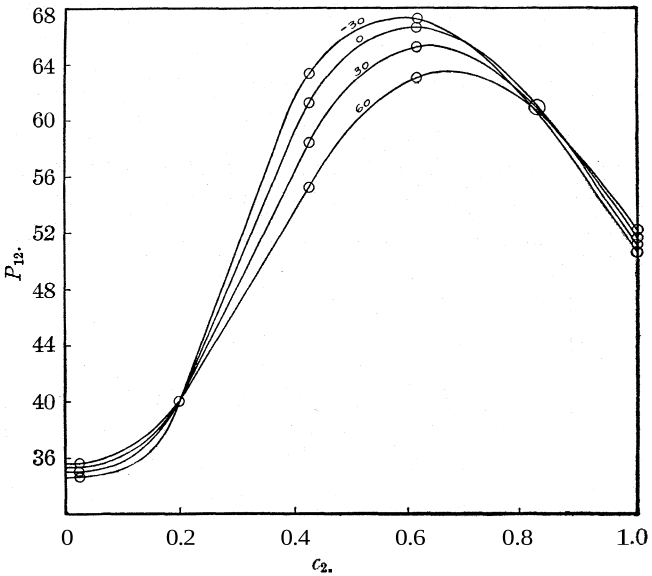

Fig. 1.—Molar polarizations (P_{12}) of heptane-ethyl alcohol mixtures.

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[3] Williams, *Z. physik. Chem.*, **138A**, 75 (1928); Mahanti and Sen Gupta, *Indian J. Phys.*, [II] *12*, 181 (1928).

ture. Just beyond this point they rise sharply, go through a maximum and finally decrease to the values for the pure alcohol. Thus, in very dilute solutions and in the pure alcohol, the polarization increases with the temperature. At intermediate concentrations the polarization decreases with rising temperature, with the result that the P_2–c_2 curves intersect both in the dilute and concentrated regions. The values of P obtained by extrapolating the P_2 curves to zero concentration of alcohol obviously

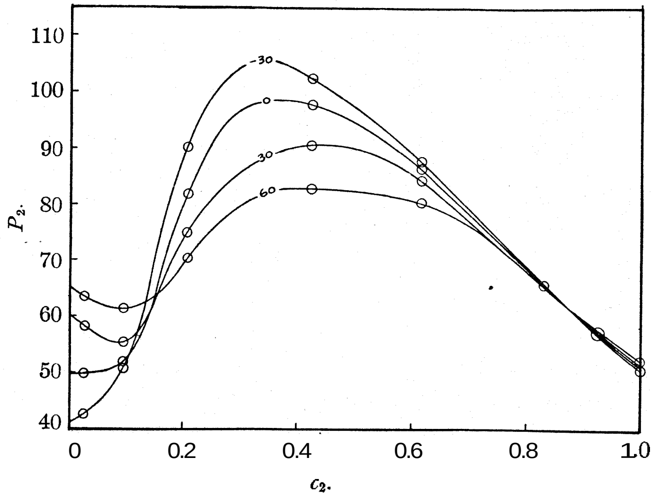

Fig. 2.—Polarizations (P_2) of ethyl alcohol in solution in hexane and in heptane.

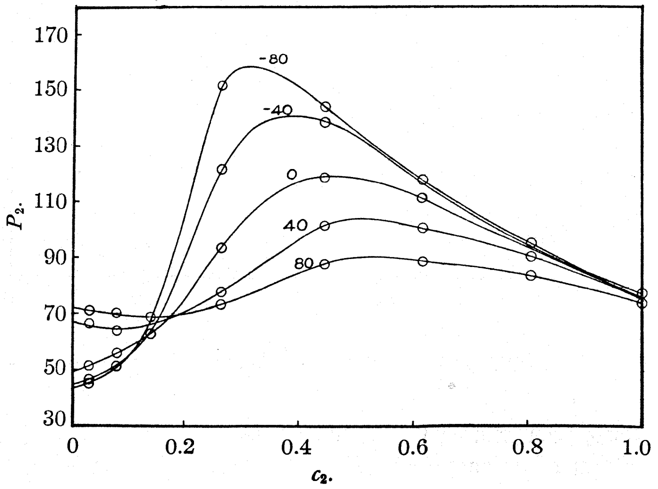

Fig. 3.—Polarizations (P_2) of butyl alcohol in solution in heptane.

do not correspond to the unassociated state, since they increase with rising temperature instead of decreasing.

The P_{12}–c_2 and the P_2–c_2 curves (Fig. 3) for butyl alcohol in heptane show a less sharply defined maximum and a greater dependence of polarization upon temperature in the concentrated solutions. For octyl alcohol in heptane, the maximum has disappeared in the P_{12}–c_2 curves (Fig. 4) and is less pronounced in the P_2–c_2 curves (Fig. 5). This decrease in the effect of orientation is also evident in the variation with temperature of the polarization in the pure alcohols. Whereas the polarization of ethyl alcohol increases with temperature over the entire range, that of butyl alcohol at first increases, then becomes practically constant and finally decreases with rising temperature. The polarization of the normal octyl alcohol, however, decreases with rising temperature over the entire temperature range within which it is measured. Another indication of this effect is given by the variation in P_M for these alcohols. The values of $P_M = P - MR_D$ at 20° for ethyl, butyl and octyl alcohols are, respectively, 38.8, 55.1 and 78.6. In dilute solution this progressive variation of the effect of orientation does not occur, the curves for the three alcohols all being quite similar.

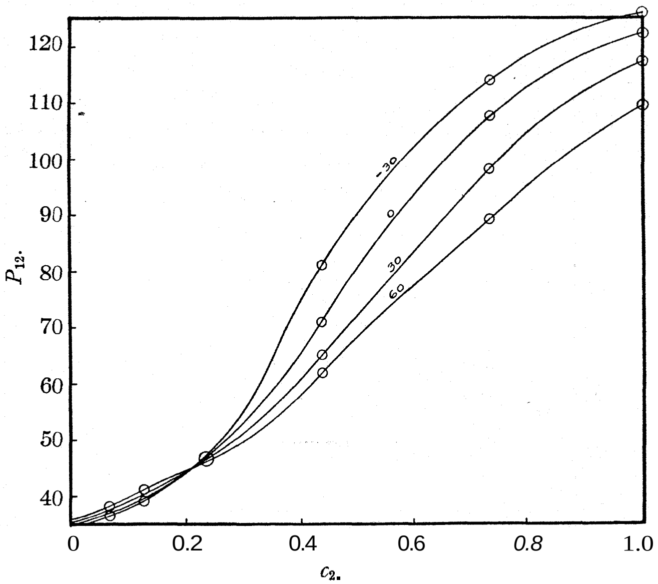

Fig. 4.—Molar polarizations (P_{12}) of heptane-*n*-octyl alcohol mixtures.

It should be explained at this point that, in the absence of a value of *a* determined from the temperature variation of P,, the small quantity P_A is neglected and *a* is set equal to MR_D, the molar refraction for the sodium D line. The error thus introduced is negligible in comparison to the uncertainties caused by molecular orientation.

These P_{12}–c_2 and P_2–c_2 curves resemble those calculated by Debye[4] from the data of Philip at 16° for solutions of ethyl alcohol in benzene in that they possess a maximum, but differ from those of Debye in that the P_2–c_2 curves generally show a minimum. The P_2–c_2 curve for butyl alcohol in benzene (Fig. 6) at 70° resembles that of Debye for ethyl alcohol, but at 50° a slight minimum appears in the region of low alcohol concentration, and at 16° it is more pronounced, showing that the same orientating influences are at work in these solutions as in those in heptane, although the intensity of the influences is somewhat less. The difference in behavior is shown by the fact that the increase in dielectric constant over that of the pure solvent is very much greater for a solution in benzene than in heptane. For example, a solution of butyl alcohol in benzene, mole fraction alcohol = 0.0525, has a dielectric constant of 2.505 at 20°. The dielectric constant of the sample of benzene used in the solution is 2.294 at 20°, and the increase in dielectric constant due to the alcohol is 2.505 − 2.294 = 0.311. The increase caused by alcohol in heptane at the same concentration and temperature is 2,001 − 1.930 = 0.071, less than one-fourth that in benzene.

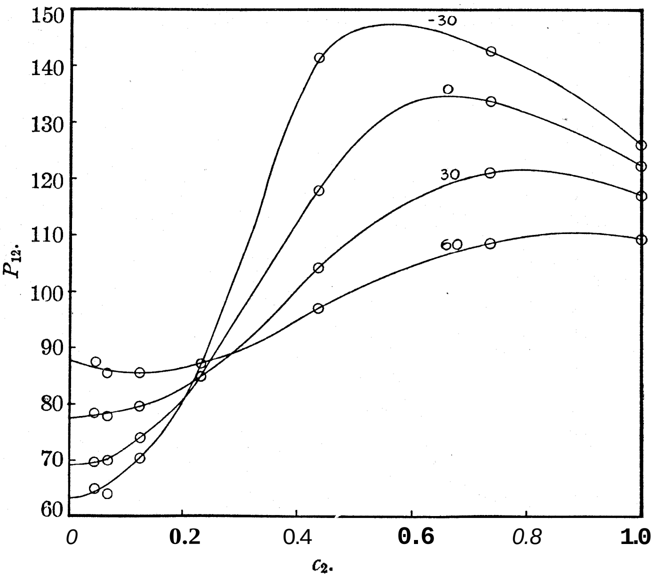

Fig. 5.—Polarizations (P_2) of n-octyl alcohol in solution in heptane.

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[4] Debye, "Polar Molecules," The Chemical Catalog Company, New York, 1929, p. 47.

The results of Lange show maxima in the curves for propyl, n-butyl and *iso*butyl alcohols in benzene with some irregularities or points of inflection in the dilute solutions, and a curve for dimethylethylcarbinol resembling in form the P_2–c_2 curves for ethyl iodide, while the two maxima appearing in the curve for iso-amyl alcohol may be attributed to the presence of two isomers in the material used for the measurements. The values of P_2 given by Krchma and Williams[5] for methyl and ethyl alcohol in solution in carbon tetrachloride at 25° indicate the presence of a minimum as well as a maximum in the curves. The course of the P_2–c_2 curves for dilute solutions of methyl alcohol in carbon tetrachloride at different temperatures determined by Stranathan[6] shows a slight minimum between 20 and 50° and a probability of intersection in a somewhat more concentrated region, the apparent value of P increasing with rising temperature. Similar curves for ethyl, propyl and iso-amyl alcohols in benzene show no minimum, but indicate the possibility of one if the measurement could be extended below 0°. They also show the usual rise toward a maximum. These results of other investigators are evidently consistent with those of the present paper.

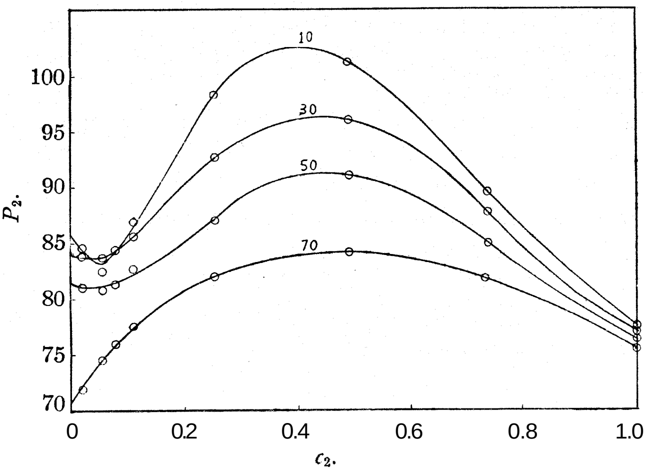

Fig. 6.—Polarizations (P_2) of butyl alcohol in solution in benzene.

In order to study further the effect of the solvent upon the variation of polarization with concentration and temperature, solutions of butyl alcohol in cyclohexane were measured. The values of P_2 check very closely with those obtained in heptane solution, showing that the effect of orientation is the same in these two solvents and somewhat different from that in benzene. It appears that in very dilute solution in heptane,

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[5] Krchma and Williams, THIS JOURNAL, 49,2408 (1927).

[6] Stranathan, Phys. *Rev.*, 31,653 (1928).

hexane, cyclohexane and carbon tetrachloride, and at lower temperatures in benzene, there is a tendency toward an orientation which decreases the polarization. With increasing concentration this tendency is soon obscured by an orientation which increases the polarization until, in the more concentrated solutions, a maximum is reached. In the most concentrated solutions the effect of orientation is to decrease the polarization once more. In the benzene, which has a slightly higher dielectric constant to weaken the forces of attraction between the solute molecules, the orientation which diminishes the polarization in the most dilute solutions is too weak at higher temperatures to be detected. It is apparent only in benzene at lower temperatures and in the other solvents at higher temperatures, being obscured or superseded in the latter at lower temperatures by the stronger tendency toward the orientation which increases the polarization. The possible mechanism of these orientations of primary alcohols will be discussed in the next paper of this series in connection with the isomers of the octyl alcohols.

The results on the solutions in benzene may be extrapolated to obtain P,, from which the moment may be calculated. The small temperature range obtainable in benzene prevents an accurate determination of the moment by plotting $P_\infty T$ against T, as was done for ethyl iodide, but b may be obtained with sufficient accuracy as (P, $- MR_D)T$ and used to calculate the values of μ shown in Table IV, which gives the results obtained at different temperatures. The values at 10° are omitted because they are more seriously affected by orientation, as in the heptane solutions.

TABLE IV

ELECTRIC MOMENTS OR ALCOHOLS CALCULATED AT DIFFERENT TEMPERATURES IN BENZENE SOLUTION

	n-C_4H_9OH ($MR_D = 22.2$)			n-$C_8H_{17}OH$ ($MR_D = 40.7$)		
T, °A.	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
293	86.3	18800	1.75	102.3	18000	1.71
303	84.1	18750	1.74	100.7	18200	1.72
313	83.2	19100	1.76	98.0	17900	1.70
323	81.0	19000	1.76	95.7	17800	1.70
333	75.5	17700	1.70	93.3	17500	1.69
343	71.0	16750	1.65	91.4	17400	1.68
		Mean,	1.74		Mean,	1.70

The approximate constancy of the values of (P, $- MR_D)T$ and μ indicate that molecular orientation is slight in the very dilute solutions in benzene. In heptane solution the polarization curves indicate that marked orientation occurs even in the most dilute solutions which can be measured. However, the values of P_2 at the highest temperatures approach closely those observed in benzene solution at the same temperatures, indicating that the effects of orientation are becoming less at high temperature. If the orientation is decreasing with rising temperature, the values of $(P, - MR_{\mathrm{D}})T$ plotted aginst T should approach a constant value. Actually the values for butyl alcohol are found to approach 17,800 asymptotically, from which the moment 1.70×10^{-18} is calculated, in good agreement with that obtained from the solutions in benzene. The **P,** values for ethyl alcohol in hexane and heptane are not as accurate as those of butyl alcohol, but the $(P, - MR_{\mathrm{D}})$T values show an approach to constancy at high temperatures, the value of the moment calculated at 60° being 1.68×10^{-18}, in excellent agreement with the values 1.74×10^{-18} obtained by Stranathan for the liquid and 1.69×10^{-18} by Miles[7] from measurements upon the vapor. The close agreement of these and other values for the moment of ethyl alcohol in the liquid state with that of Miles for the vapor shows the incorrectness of Sanger's[8] value 1.1×10^{-18} for the vapor. These results taken in conjunction with those of the other investigators to whom reference has been made indicate that the moments of the primary alcohols differ from a value of 1.68×10^{-18} by no more than the experimental error. It may, therefore, be concluded that the electric moment of the molecule of a primary alcohol is independent of the length of the carbon chain.

Summary

The dielectric constants and densities of solutions of ethyl iodide in heptane and of ethanol, n-butanol and n-octanol in a number of non-polar liquids have been measured over a wide range of temperature and concentration. A qualitative indication of the anomalous dispersion and absorption for a wave length of 600 meters has been obtained for the pure alcohols and their solutions.

The dielectric polarizations of ethyl iodide give further evidence of the applicability of the Debye equation to liquids in very dilute solution. The polarizations of the alcohols are greatly affected by molecular orientation, being increased in some regions of temperature and concentration and decreased in others. These complicated effects of orientation interfere with the exact application of the Debye equation, but do not prevent the calculation of the electric moments of the molecules.

It is concluded that the electric moment of the molecule of a primary alcohol is independent of the length of the carbon chain.

PRINCETON, NEW JERSEY

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[7] Miles, private communication to the authors.

[8] Sänger, *Physik. Z.*, 28,455 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. VII. ISOMERIC OCTYL ALCOHOLS AND MOLECULAR ORIENTATION

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As the material in the preceding paper of this series showed the exceedingly complicated effect of molecular orientation upon the polarization of primary alcohols, it seemed important to study the variation of this effect with variation in the position of the hydroxyl group in the molecule and with branching of the carbon chain. The preparation of twenty-two isomers of octyl alcohol by Dr. H. B. Glass, Dr. G. B. Malone and Dr. G. L. Dorough working with Prof. E. Emmet Reid of Johns Hopkins University has given an exceptional opportunity for studying the dependence of dielectric behavior upon these factors. The quantities of material available have not been sufficient to permit of measurements in solution except in the cases of octanol-1, which has been treated in the preceding paper, and 2-methylheptanol-3, but preliminary conclusions may be drawn from the behavior of the pure liquids, taken in conjunction with that of the two very different octyl alcohols in solution, and it is expected that more measurements in solution will be possible in the near future.

The measurements were carried out in the manner described in the previous paper, the dielectric constants being determined with a capacity bridge at a wave length of 600 meters. Table I gives the densities, d, and dielectric constants, ϵ, of solutions of 2-methylheptanol-3 in benzene obtained at 10° intervals by graphical interpolation from measurements made at 10 to 20° intervals, and the polarizations, P_2, of the alcohol calculated from them. The polarizations are shown graphically in Figs. 1 and 2. In the pure alcohols at low temperatures, anomalous dispersion and absorption made it necessary to increase the series resistance in the balancing arm of the bridge, which was used to compensate for conductance in the measuring cell. The introduction of large resistances so reduced the accuracy of the dielectric constant measurements that the values at these low temperatures are sometimes given to only one decimal place in Table II, which also gives the value of the compensating resistance R in ohms as a rough indication of the magnitude of the absorption. A resistance of an ohm or less may be regarded as indicative of a negligible effect and it is only when the resistance approaches 10 ohms or more that the absorption may be regarded as considerable. In the case of 2-methylheptanol-2, the compensating resistance increased somewhat at higher temperatures because of slight decomposition and resulting conductance in the liquid. That the effect of this decomposition on the dielectric constant was negligible was shown by the last value obtained for the liquid after cooling down again to 19.1°. The high resistance required for 5-methylheptanol-2 was the result of rapid decomposition of the liquid, which made the values of ϵ very uncertain. Because of the effect of molecular orientation, the dielectric constants of several of the alcohols decrease with decreasing temperature instead of increasing in accordance

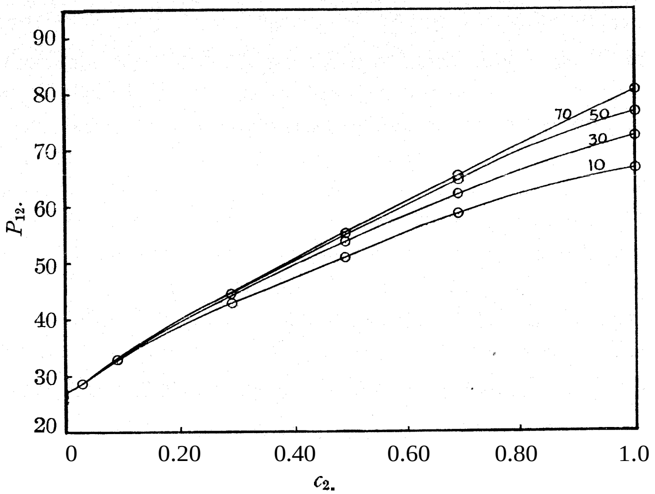

Fig. 1.—Molar polarizations (P_{12}) of benzene-2-methylheptanol-3 mixtures.

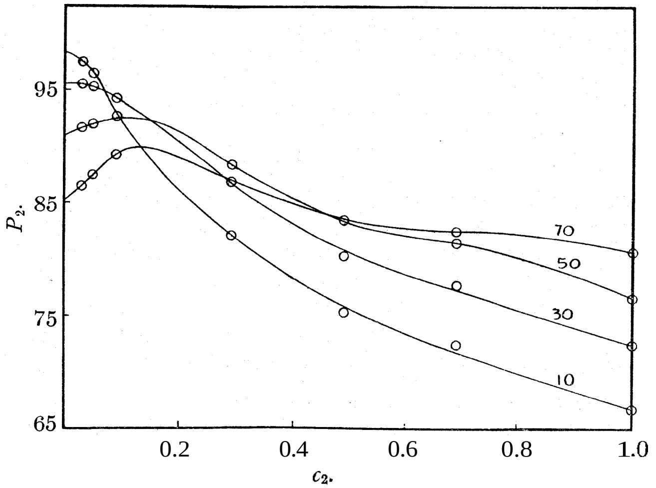

Fig. 2.—Polarizations (P_2) of 2-methylheptanol-3 in solution in benzene.

with the Debye equation, but it is only in a few cases that the measurements have been carried to temperatures at which the anomalous dispersion is sufficient to cause a measurable lowering of dielectric constant with decreasing temperature.

In Table III are given the polarizations of twenty isomeric octyl alcohols which are represented as methylheptanols, the first number at the top of each pair of columns indicating the position of the methyl group and the second that of the hydroxyl. The only methylheptanols omitted are 2-methylheptanol-3, given in Table I, and 5-methylheptanol-2, which decomposed too rapidly in the cell to give reliable results. The densities used in the calculation of the polarizations were obtained by linear extrapolation of the values at 0 and 25° determined by Dr. G. B. Malone. Since the densities of ethyl, n-butyl and n-octyl alcohols are practically linear functions of temperature below 25°, the use of these extrapolated values should not introduce serious error in the polarizations, which

TABLE I

INTERPOLATED VALUES OF DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF 2-METHYLHEPTANOL-3 IN BENZENE AND POLARIZATIONS OF COMPONENTS

Mole fr. $C_8H_{17}OH$ = t, °C.		0.0303	0.0331	0.0398	0.0502	0.0662	0.0889	0.2915	0.4892	0.6915	1.000
0								2.926	3.077	3.160	3.09
10		2.418	2.428	2.451	2.482	2.530	2.589	2.961	3.154	3.263	3.23
20		2.394	2.402	2.424	2.458	2.506	2.569	2.987	3.214	3.354	3.37
30		2.368	2.376	2.397	2.430	2.479	2.545	2.994	3.253	3.429	3.50
40		2.341	2.350	2.368	2.400	2.448	2.515	2.984	3.280	3.486	3.60
50		2.313	2.322	2.339	2.369	2.415	2.480	2.955	3.274	3.521	3.68
60		2.284	2.295	2.308	2.336	2.380	2.443	2.908	3.242	3.514	3.75
70		2.255	2.267	2.277	2.304	2.345	2.406	2.849	3.192	3.465	
						d					
0								0.8702	0.8585	0.8497	0.8400
10		0.8861	0.8858	0.8846	0.8835	0.8820	0.8791	.8608	.8494	.8411	.8324
20		.8754	.8752	.8740	.8730	.8714	.8687	.8512	.8404	.8323	.8248
30		.8648	.8645	.8633	.8624	.8607	.8581	.8419	.8313	.8236	.8168
40		.8541	.8537	.8527	.8517	.8500	.8475	.8324	.8221	.8150	.8084
50		.8435	.8431	.8422	.8411	.8396	.8372	.8229	.8129	.8063	.7996
60		.8327	.8322	.8315	.8304	.8288	.8266	.8130	.8034	.7984	.7910
70		.8220	.8215	.8206	.8198	.8182	.8160	.8029	.7939	.7885	.7823
	$P_1(C_6H_6)$					$P_2(C_8H_{17}OH)$					
0								79.0	70.2	69.4	63.5
10	26.69	97.6	97.7	97.8	96.4	95.1	92.8	82.1	75.3	72.6	66.7
20	26.72	97.2	96.6	96.8	96.4	95.2	93.7	84.7	78.0	75.2	69.6
30	26.75	95.6	95.3	95.5	95.3	95.0	94.2	86.7	80.2	77.7	72.4
40	26.78	93.4	93.8	93.4	93.6	93.8	93.7	87.9	82.1	79.8	74.6
50	26.78	91.4	92.0	91.6	92.0	92.3	92.5	88.3	83.2	81.5	76.7
60	26.78	88.8	90.5	89.1	89.6	90.3	91.0	87.9	83.6	82.5	78.6
70	26.76	86.4	89.3	86.9	87.6	88.3	89.3	87.0	83.5	82.5	

are probably accurate within 0.5 to 2.0%. For example, the polarization of 2-methylheptanol-3 calculated from the extrapolated density is 78.3 at 60° while that calculated from the interpolation of our own measurements in Table I is 78.6, no difference at all being found at 40°.

TABLE II

DIELECTRIC CONSTANTS AND COMPENSATING RESISTANCES FOR OCTYL ALCOHOLS

t, °C.	ϵ	R
Octanol-1		
−4.4	12.71	4.0
8.6	11.42	2.4
19.1	10.39	1.9
32 1	9.34	1.8
44.6	8.18	1.8
58.2	7.20	1.8
Octanol-4		
−31.1	8.97	28.5
−21.1	7.88	7.4
− 9.6	6.66	1.8
2 5	5.83	0.6
15.6	5.26	.3
27.9	4.91	.2
41.1	4.72	.2
55.2	4.51	.2
4-Methylheptanol-1		
−36.6	7.36	7.3
−36.3	7.49	12.3
−31.2	7.48	7.3
−17.8	6.22	2.6
− 7.0	5.59	1.6
0.0	5.30	0.9
5.3	4.99	.5
17.4	4.63	.4
29.8	4.24	.4
43.7	3.95	.4
59.0	3.73	.4
6-Methylheptanol-2		
−46.0	6.8	63.8
−42.3	9.6	88
−34.2	11.35	12.8
−25.2	10.95	5.2
−16.6	9.87	2.4
− 7.3	8.75	1.2
4.9	7.18	0.7
16.9	6.41	.5
29.0	5.67	.4
41.6	5.10	.4
55.5	4.68	.4
Octanol-2		
−37.9	13.03	19.2
−30.3	14.64	10.0
−21.5	13.61	4.3
− 9.1	11.86	1.6
3.0	10.51	0.8
15 7	8.68	.6
29.8	7.30	.5
43.5	6.28	.4
56.3	5.60	.4
6-Methylheptanol-1		
−45.2	15 13	14.9
−33.5	15.25	5.6
−20.9	14.27	2.4
− 8.1	12.96	1.4
4.4	11.75	1.1
17.1	10.54	1.0
29.4	9.40	1.0
42.2	8.31	1.1
55.0	7.41	1.1
3-Methylheptanol-1		
−32.0	3.239	1.5
−19.6	3.116	0.7
− 7.5	3.022	.5
4.9	2.946	.4
17.1	2.884	.4
29.5	2.827	.3
42.4	2.786	
55.6	2.747	
2-Methylheptanol-1		
−46.2	8.58	21.0
−37.6	9.47	10.7
−28.6	8.85	4.6
−19.2	8.14	2.2
− 7.8	6.96	1.1
5.8	5.89	0.6
19.8	5.16	.5
29.6	4.78	.4
42.0	4.43	.4
54.9	4.15	.4
2-Methylheptanol-4		
−43.7	2.68	5.5
−34.3	2.83	3.9
−24.7	2.91	1.6
−11.4	2.991	0.7
− 1.3	3.081	.5
10.8	3.203	.4
23.1	3.338	.4
35.6	3.469	.4
48.1	3.574	.5
59.5	3.645	.5
2-Methylheptanol-2		
−48.5	3.36	15.5
−41.0	3.55	7.8
−32.6	3.49	2.7
−22.6	3.42	1.1
−13.1	3.38	0.6
− 6.6	3.38	.5
− 0.5	3.39	.5
5.5	3.40	.5
15.0	3.43	.5
28.5	3.47	.7
41.6	3.51	1.2
50.9	3.54	2.1
60.3	3.54	5.2
19.1	3.45	1.0
4-Methylheptanol-2		
−43.3	5.0	79.0
−37.9	5.7	60.9
−33.4	5.6	35.5
−26.6	5.1	13.8
−18.4	4.6	4.3
−10.6	4.22	1.5
− 0.3	3.90	0.8
7.8	3.77	.5
16.8	3.65	.5
25.7	3.59	.5
35.0	3.54	.4
48.0	3.48	.5
60.0	3.36	.5

TABLE II *(Concluded)*

t, °C.	ϵ	R
Octanol-3		
−27.3	10.5	4.9
−19.6	9.83	2.6
−8.5	9.03	1.4
2.6	8.01	0.9
15.2	7.26	.8
27.9	6.65	.8
42.5	6.06	.8
54.0	5.68	.7
3-Methylheptanol-2		
−44.4	10.8	2.1
−32.8	9.9	1.2
−20.6	9.17	1.0
−8.1	8.52	1.0
4.6	7.94	1.1
16.4	7.47	1.1
29.0	7.00	1.2
42.0	6.60	1.2
55.6	6.21	1.2
5-Methylheptanol-1		
−38.1	12.67	10.0
−28.3	11.79	4.4
−19.2	10.98	2.4
−6.6	9.69	1.4
5.0	8.65	1.1
17.2	7.68	1.0
29.6	6.79	1.0
42.8	5.96	0.9
55.0	5.37	0.9
5-Methylheptanol-3		
−42.7	8.58	1.0
−32.5	8.04	0.7
−20.0	7.48	.7
−8.1	7.01	.7
4.2	6.60	.8
17.7	6.20	.8
30.6	5.85	.9
42.2	5.57	.9
56.5	5.25	.9
3-Methylheptanol-3		
−41.7	3.60	5.0
−30.8	3.58	1.5
−19.4	3.57	0.7
−7.5	3.593	.5
0.6	3.624	.5
7.0	3.657	.4
13.5	3.694	.4
22.2	3.755	.4
31.3	3.796	.4
41.3	3.843	.5
50.8	3.878	.5
59.9	3.894	.5
3-Methylheptanol-4		
−43.1	10.37	0.9
−38.1	10.10	.7
−30.3	9.63	.6
−22.2	9.20	.5
−13.7	8.79	.5
−4.1	8.30	.5
5.0	7.91	.5
16.8	7.46	.5
29.2	7.04	.5
41.5	6.66	.5
56.5	6.21	.6
22.5	7.25	.6
4-Methylheptanol-4		
−43.8	2.528	1.0
−38.2	2.531	0.6
−30.7	2.550	.4
−22.0	2.557	.4
−13.7	2.611	.3
−1.1	2.688	.3
11.5	2.790	.3
23.0	2.902	.3
35.4	3.037	.3
48.2	3.167	.4
54.1	3.221	.4
60.4	3.270	.4
2-Methylheptanol-3		
−41.4	2.70	3.0
−34.0	2.76	1.7
−24.7	2.83	0.8
−12.4	2.953	.5
−1.2	3.087	.4
10.8	3.245	.4
23.6	3.418	.4
35.3	3.554	.4
47.8	3.669	.4
60.4	3.754	.4
4-Methylheptanol-3		
−52.5	7.11	1.1
−43.2	7.04	0.7
−30.8	6.60	.5
−19.0	6.22	.5
−8.3	5.90	.4
4.7	5.59	.4
17.2	5.31	.3
29.6	5.05	.3
42.3	4.80	.3
55.6	4.61	.3
5-Methylheptanol-2		
−43.0	10.6	14.5
−31.8	9.6	13.7
−18.1	8.6	16.3
−6.8	8.0	19.4
5.3	7.5	23.1
6-Methylheptanol-3		
−42.6	8.76	3.8
−32.0	7.79	1.7
−19.4	7.13	1.0
−7.3	6.53	0.6
5.3	6.12	.5
17.4	5.56	.4
29.8	5.18	.4
29.5	5.27	.4
42.6	4.95	.4
55.5	4.67	.4

When the polarizations, P_{12}, of the mixtures of 2-methylheptanol-3 in benzene are plotted against c_2, the mole fractions of the alcohol, the curves obtained (Fig. 1) show so little deviation from the theoretical linearity as to suggest that molecular orientation in the mixtures is slight. When P_2, the polarization of the alcohol, is plotted similarly against c_2, curves are obtained (Fig. 2) which, if only one or two concentrations

TABLE III

POLARIZATIONS OF THE METHYLHEPTANOLS

t, °C	7-1	7-2	7-3	7-4	6-1	5-1	4-1
−50						121	
−40		118.2			124.8	121	104
−30		124.4	115.2	109.6	125.3	120	105
−20		123.1	114.3	105.8	124.7	118	99
−10	123.7	121.4	112.7	101.2	123.8	116	95
0	122.5	118.7	110.0	97.5	122.9	114	93
10	121.0	115.3	108.1	93.6	121.3	111	90
20	119.3	111.9	105.7	91.6	119.8	108	86.7
30	117.3	108.4	104.2	90.5	117.4	106	84.1
40	115.1	104.4	100.8	89.3	115.1	102	82.1
50	112.5	101.0	100.1	88.9	111.8	99	81.9
60	109.4	97.7	99.7	88.6	109.8	95	79.2

t, °C.	3-1	2-1	6-2	4-2	3-2	2-2	6-3
−50	69.6				115		
−40	68.4	113	118	93	114	69.8	111
−30	66.9	113	119	92	112	69.3	110
−20	65.9	110	117	86	111	69.0	108
−10	64.9	106	114	81	110	69.1	106
0	64.2	102	110	78.3	109.4	70.0	104
10	63.6	97	106	76.6	108.4	71.1	102
20	63.2	94.2	102	75.6	107.4	72.1	101
30	62.9	91.1	99	75.4	106.4	73.5	99
40	62.8	88.6	95	75.3	104.3	74.8	97
50	62.8	86.7	93	75.2	104.5	75.9	96
60	62.8	85.1	91	74.1	103.5	76.7	95

t, °C.	5-3	4-3	3-3	2-3	4-4	3-4	2-4
−50		103	68.2	52.4	49.9		
−40	106	102	68.6	54.3	50.4	111	56.9
−30	105	101	69.1	56.3	51.1	110	58.8
−20	104	100	69.5	59.1	52.5	109	60.6
−10	103	99	70.3	61.1	54.0	108	62.5
0	102	98	71.6	63.5	56.0	107	64.5
10	101	97	73.0	66.7	58.2	106	67.0
20	100	95.6	74.6	69.6	60.6	105	69.4
30	99	94.7	76.2	72.4	63.1	104	71.9
40	98	94.0	77.5	74.6	65.7	104	74.0
50	97	93	78.9	76.5	68.4	103	76.0
60	96	91	79.9	78.3	70.7	102	77.8

and one temperature had been measured in the dilute region, would have been extrapolated to $c_2 = 0$ in a shape resembling the P_2–c_2 curves given by ethyl bromide or ethyl iodide, the polarization increasing more and more rapidly up to infinite dilution. Moreover, the value of the moment calculated from the value of P_∞ by subtracting the molar refraction, MR_D, would not have been seriously in error. However, the determination of a number of points in the dilute region makes it clear that the curves possess a maximum or, at least, a tendency toward one, which is much less prominent than in the curves for the primary alcohols in the preceding paper. The curves in the dilute region given on a larger scale in Fig. 3 are linear at the higher temperatures. The values of P_∞ obtained as their intercepts at $c_2 = 0$ are given in Table IV and used to calculate the values of the moment μ shown in the last column. The slight decrease in $(P_\infty - MR_D)T$ and μ with rising temperature may indicate that the effect of orientation is not wholly eliminated by the extrapolation, but the mean value 1.62×10^{-18} is certainly not far from correct.

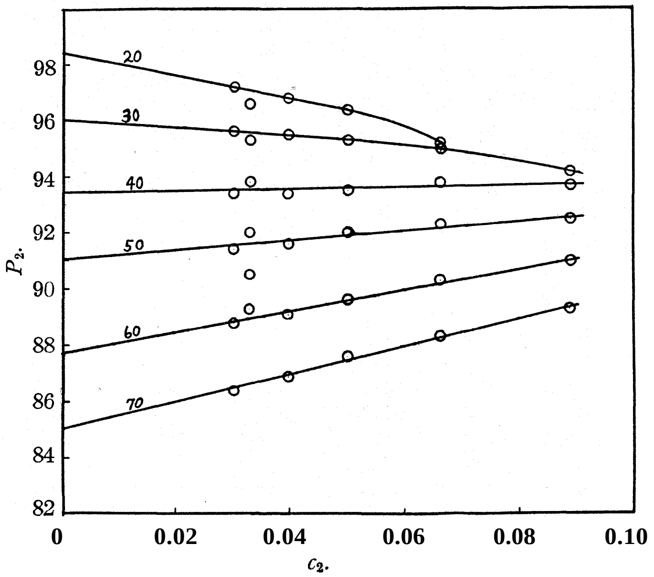

Fig. 3.—Polarizations (P_2) of 2-methylheptanol-3 in benzene solution.

TABLE IV

ELECTRIC MOMENT OF 2-METHYLHEPTANOL-3 CALCULATED AT DIFFERENT TEMPERATURES ($MR_D = 40.5$)

T, °A.	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
293	98.4	16900	1.66
303	96.0	16800	1.65
313	93.5	16600	1.64
323	91.0	16300	1.62
333	87.7	15700	1.60
343	85.0	15300	1.57
		Mean =	1.62

The moment of 2-methylheptanol-3 appears to be slightly lower than that of octanol-1, although the difference may be the result of error caused by molecular orientation. It has been shown that the electric doublet in the alcohol molecules lies at the hydroxyl group and really consists of two doublets, the resultant of which gives the observed moment.[1] This, taken in conjunction with the fact that the moments of the primary alcohols are practically independent of the length of the carbon chain, at least, up to eight carbon atoms, leads one to expect the differences in moment among the octyl alcohols to be small, as in the case of the two just considered. The dielectric constants at 20° of the nine isomeric heptanes, which have no moments, differ from 1.93 by no more than 0.015 and their polarizations, which consist of P_E plus a very small P_A, differ from 34.50 by no more than 0.26.[2] The molar refractions, MR_D of the twenty-two isomeric octyl alcohols determined by Dr. H. B. Glass differ from 40.90 by no more than 1.30. As the polarization is made up of P_M, the contribution of the moment, P_E, the electronic contribution, which differs from MR_D by hardly one unit, and the small P_A, the polarizations of the different isomers should be nearly the same in the absence of molecular orientation. From these values of the moment and the refraction, the polarization at 25° is calculated to be approximately 100 and the dielectric constant, 5.4. Marked deviations from these values are to be attributed to the effect of molecular orientation.

The orienting effect of the molecules of a liquid upon one another must depend not only on the size of their doublets, but also upon the location of the doublet or doublets in the molecule, and upon the mere geometrical shape of the molecule. There are two possible simple orientations which two doublets in adjacent molecules may be expected to adopt relative to one another. The negative end of one doublet may attract the positive end of the other so that the axes of the two doublets fall in line and the two support one another. This will be referred to as an orientation of the first type. The two molecules may associate to act as one, but, if they do not, they should still attract one another and tend to orient more or less with respect to one another so that, when a field is applied externally to measure the dielectric constant, the orientation would be greater than that calculated, and the polarization would be abnormally higher. The shape of the molecules would commonly prevent an exact lining up of the doublets and their axes would, consequently, make an angle of somewhat less than 180° with one another. As this angle decreases, the polarization diminishes and the common effect of orientation is to decrease the polarization instead of increasing it. When the angle between the axes becomes zero, that is, when the doublets are parallel and pointing in opposite directions, the moments cancel one another and the doublet contribution to the polarization becomes zero. This position of

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[1] Smyth, THIS JOURNAL, 46,2151 (1924).

[2] Smyth and Stoops. *ibid.,* 50, 1883 (1928).

the doublets, which will be referred to as the second type of orientation, would result in a polarization for a polar substance differing little from its molar refraction. More than two molecules may line up if the first type of orientation prevails and one may imagine a high polarization built up in this way. The stability of the orientation of one molecule relative to another must depend to some extent upon the forces exerted upon it by the other neighboring molecules. It appears probable, therefore, that, when there is not much difference between the energies of two different orientations, one orientation may change to the other as the mean distance between the dipole molecules changes. Thus, when a polar liquid is dissolved in a non-polar, the orientation of the polar molecules relative to one another may change from one type to another with change in concentration. Of course, when the polar molecules are in very dilute solution and, on the average, far away from one another, they should assume a random orientation unless they actually associate to form a definite complex molecule which is not much dissociated even in the dilute solution, as appears to be the case with acetic acid in benzene solution. Change in temperature also might affect the type of orientation.

The interaction of the dipoles in the majority of liquids decreases the polarization in the manner of the first type of orientation, but hydroxyl doublets lie close to the surface of the molecule and produce a strong localized external field. Molecules of the formula ROH may hypothetically be fitted together in such a way as to arrange the doublets according to either type of orientation. The structure of the associated alcohol molecules proposed by Sidgwick[3] would correspond to the first type, but, on paper at least, a double molecule corresponding to the second type may be equally easily obtained. The somewhat hazardous juggling of these formulas on paper has been treated briefly by one of the authors in *a* paper to appear shortly.

The variation of the polarization of the alcohols with concentration and temperature is so complicated that the correctness of a detailed explanation in terms of orientation cannot be assured, but there are certain obvious facts upon which a possible explanation may be founded. An orientation of the first type must occur to some extent in order to cause the maximum observed in the P_2–c_2 curves. The approximate conformity of the polarizations in the very dilute benzene solutions to the Debye equation and the excellent agreement of the moments obtained from them with the values obtained for several of the alcohols in the vapor state show that in these solutions the alcohol molecules must be nearly all single and oriented practically at random. The approach to the correct values of P_∞ in the heptane solutions at the highest temperatures indi-

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[3] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, Oxford, 1927, p. 134.

cates an existence mainly as single molecules oriented at random in the most dilute solutions at high temperatures in heptane, which, with its lower dielectric constant, has less dissociating power than benzene. With increasing concentration in the very dilute solutions, these single dipole molecules acting upon one another appear to bring about an orientation of the second type, by which the polarization is decreased, as in the case of ethyl iodide and ethyl bromide. As this effect is increased by decreasing temperature, it is so strong even in the very dilute heptane solutions of the primary alcohols as to make the extrapolated values, P,, decrease with decreasing temperature instead of increasing as required by the Debye equation. At the same time, however, molecules are coming together and orienting according to the first type, probably forming aggregates and tending to increase the polarization. At the low temperatures in heptane this effect more than counterbalances the decrease in polarization with increasing concentration in the very dilute solutions, which has just been discussed; at the high temperatures in benzene it does so as well, since here the effect of the single molecules upon one another is small. At the lower temperatures in benzene and the higher in heptane, this latter effect for a short range of concentration more than counterbalances the increase in polarization caused by the formation of the aggregates. Since the formation of aggregates must be greater the lower the temperature, the rate of increase of the polarization with concentration is also greater the lower the temperature and the maximum reached is higher. As the concentration of these aggregates increases, they may act upon one another as the single molecules are supposed to do in the very dilute solutions. This effect opposes the increase in polarization due to the formation of more aggregates with increasing concentration and becomes stronger and stronger so that the polarization passes through a maximum and decreases. The effect is greater the lower the temperature, with the result that the decrease in polarization is greater, the curves intersect, and the polarization of the pure liquid is lower at the lower temperatures in the case of ethyl alcohol. In the case of butyl alcohol, in which the longer carbon chain produces a greater mean separation of the doublets, the polarization of the pure liquid decreases with temperature only at the lower temperatures, and in %-octyl alcohol, where the separation or insulation of the doublets is still greater, it increases with decreasing temperature down to the region of anomalous dispersion. The interaction of the molecular aggregates in producing an effect equivalent to that of the second type of orientation may be treated in terms of the potential energy of the system. The increase of orientation of the first type with increasing concentration should increase the field surrounding the dipole molecules and thus increase the potential energy. If this increase in potential energy is sufficiently great, the resulting instability may cause a change to orientation of the second type with resulting decrease in polarization.

In 2-methylheptanol-3 the hydroxyl doublet is near the middle of a branched carbon chain, which should partially screen it, reduce the external field due to it, and so lessen the chances for orientation of the first type. In the dilute solutions in benzene at high temperatures, the formation of aggregates is sufficient to increase the polarization with increasing concentration over a short range, but, at lower temperatures and at higher concentrations, the orientation of the second type predominates over the rather weak tendency to form aggregates with orientation of the first type. The polarization therefore decreases with decreasing temperature and increasing concentration. So great is the effect that not only the polarization but also the dielectric constant increases with rising temperature, and this is found to be true of all the tertiary and several of the secondary octyl alcohols measured.

In the majority of cases where an abnormally high dielectric constant indicates that the alcohol molecules are probably forming aggregates in an orientation of the first type, the x-ray diffraction measurements of Professor G. W. Stewart, who has very kindly made his results available to us, point to the existence of double molecules, while the x-rays indicate single molecules in the majority of cases in which the low dielectric constant is attributed to the interaction of single molecules in an orientation of the second type. There are exceptions, however, as is true also of the anomalous dispersion and absorption.

The tendency toward anomalous dispersion and absorption is greater in those alcohols which are indicated by high dielectric constants as forming molecular aggregates with orientation of the first type, which would be expected from the dependence of the dispersion and absorption upon the cube of the molecular radius. It is a striking fact that, of the ten methylheptanols which show little or no absorption at the temperatures investigated, eight have either the methyl or the hydroxyl on the third carbon, and the only alcohol with the third carbon occupied by methyl or hydroxyl to show absorption is octanol-3, in which it is less pronounced than in any of the other three octanols. All of these alcohols which show little or no tendency toward dispersion and absorption are indicated by the x-ray measurements as existing as single molecules. 2-Methylheptanol-2 has a low dielectric constant, which at low temperatures above the region of anomalous dispersion decreases with rising temperature and then increases, indicating an orientation of the second type. However, the x-rays indicate existence in double molecules and, in conformity with this, it shows a marked tendency toward anomalous dispersion and absorption. It seems probable, therefore, that the molecules of this substance tend to double up in an orientation of the second type, in which the dipoles oppose one another. It is obvious that our ignorance of the details of the molecular shapes renders impossible the accurate prediction of properties which must be strongly influenced by them, hut it appears to be possible to explain, in qualitative fashion, the complex dielectric behavior of the alcohols on the basis of simple and not unreasonable assumptions.

Summary

The dielectric constants of twenty-two isomeric octyl alcohols have been measured over a wide range of temperature and an indication of their tendency toward anomalous dispersion and absorption for a wave length of 600 meters has been obtained.

Solutions of 2-methylheptanol-3 in benzene have been measured in order to obtain the electric moment of the molecule, which is close to that of *n*-octyl alcohol and the lower alcohols.

The great differences among the dielectric constants of the isomers are attributed to the effects of molecular orientation, which causes the dielectric constants of the tertiary methylheptanols and two of the secondary to increase with rising temperature instead of decreasing in the normal manner.

The explanation of the values of the dielectric constants in terms of molecular orientation is consistent with the observed tendencies toward anomalous dispersion and absorption and with the results of the x-ray diffraction measurements of Stewart.

PRINCETON, NEW JERSEY

[CONTRIBUTION NO. 610 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

CHEMICAL KINETICS IN HIGHLY DILUTE SOLUTION. BROMO-ACETATE AND THIOSULFATE IONS IN THE PRESENCE OF SODIUM ION AT 25°

BY VICTOR K. LA MER[1]

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It has been shown by Slator[2], as well as others,[3] that reactions of the type

$$BrCH_2COO^- + S_2O_3^{--} \longrightarrow S_2O_3CH_2COO^{--} + Br^- \qquad (1)$$

in which a halogen is replaced by thiosulfate are bimolecular and singularly free from side reactions. Since thiosulfate can be determined with great precision and comparative ease, reactions of this type are particularly well adapted for testing quantitatively, theories of salts catalysis, since the reaction rate can be followed very accurately in the region of high

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[1] Paper presented at the Minneapolis Meeting of the American Chemical Society, September, 1929.

[2] Slator, J. *Chem. Soc.*, *87,* 485 (1905), and earlier papers.

[3] Krapivin, *Z. physik. Chem., 82,* 439 (1913); see also J. *Chim. Phys., 10, No.* 2, 289 (1912), for data on the chloro-acetate reaction.

dilution. In addition no change in ionic strength occurs during the progress of the reaction. In this paper we shall present preliminary data for the reaction rate in the presence of sodium ion by extending the data of Krapivin[3] at 25° from a concentration of 0.01 N (0.025μ) to concentration as low as 0.0005 N (0.00125μ).

According to Brönsted,[4] a bimolecular reaction follows the scheme

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{X} \longrightarrow \text{Resultants} \tag{2}$$

where X is a critical collision complex of great instability whose charge Z_X should equal the algebraic sum of the charges on the reactants; namely, $Z_\mathrm{X} = Z_\mathrm{A} + Z_\mathrm{B}$. The general velocity equation for Scheme I becomes

$$\frac{-\mathrm{d}x}{\mathrm{d}t} = k_0 \times C_\mathrm{A} \times C_\mathrm{B} \times \frac{f_\mathrm{A} \times f_\mathrm{B}}{f_\mathrm{X}} \tag{3}$$

where k_0 is the true velocity constant independent of salt effects for a given reference medium and the factor $F_\mathrm{A} = f_\mathrm{A} \times f_\mathrm{B}/f_\mathrm{X}$ takes account of the change in velocity with changing environment.

Inasmuch as *individual ion* activities like f_A and f_B are not accessible to direct measurement owing to uncertainties in liquid junction potentials, and particularly since the very fugitive nature of X itself precludes any attempt to determine the individual behavior of f_X by any of the customary thermodynamic methods, it is evident that the quantitative verification of this theory must be obtained in the region of such highly dilute solutions that the activity coefficients of the individual ions may reasonably be expected to follow the Debye-Hückel[5] limiting law, *i. e.*, they are determined solely by the valence type and the concentration.

Although the colorimetric and conductimetric experiments of Bronsted and Livingston[6] furnish the most striking and most convincing evidence that Equation **3** is correct in principle, yet owing to irregularities in the data one cannot state definitely whether the discrepancies which they observed from the behavior predicted by the Debye limiting law arise primarily from unavoidable experimental errors or whether the deviations really represent specific individual properties which do not vanish completely in the concentration range $\mu = 0.00135$ to 0.01. In fact, the authors are careful to point out that "the character of these deviations is of great interest in the study of chemical kinetics, and ought to be the object of a more careful investigation." When we recognize that the critical complex in their Reaction II is of the tetravalent type, and that the activity coefficients of trivalent ions do not follow the limiting law even qualitatively at dilutions as low as 0.001μ in the presence of divalent ions

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[4] (a) Brönsted, Z. *physik. Chem.*, 102, 169 (1922); (b) 115, 337 (1925); (c) Columbia University Lectures, "Contemporary Developments in Chemistry," March, 1927.

[5] (a) Debye and Hückel, *Physik.* Z., 24, 185 (1923); (b) Bronsted and La Mer, THIS JOURNAL, 46, 555 (1924); *(c)* La Mer, *Trans. Am. Electrochem. Soc.*, 61, 631 (1927).

[6] Brönsted and Livingston, THIS JOURNAL, 49, 435 (1927).

of opposite sign, as has been shown in numerous recent publications from this Laboratory,[7] it would not have been surprising if still more conspicuous deviations had intruded. That they do not appears to be due to the fact that the authors' choice of solvents was such that the ions of opposite sign were always of the univalent type.

Before extending our kinetic studies to include the complications of high valence ions of opposite sign, it seemed advisable to prove that Reaction I actually obeys the Debye limiting law when the ion of opposite sign is univalent. While these experiments were in progress, a paper by Kappana,[8] working under the direction of J. C. Ghosh, has appeared in which the same reaction is followed at 30, 40 and 50° for the primary purpose of proving that the temperature coefficient is practically independent of the salt concentration, as predicted by the theories of Debye and of Ghosh and which make it desirable to record our results without further delay.

Experimental

The reaction was followed by mixing equivalent quantities of dilute solutions of sodium thiosulfate and sodium bromo-acetate in a thermostat kept at 25 ± 0.005° and removing appropriate aliquots (10–25 cc.) at definite time intervals. The reaction was stopped by adding excess iodine solution followed by back titration with thiosulfate. In the more dilute solutions (See Tables I and II), where the half time of the reaction is slow (about 55 hours at 0.001 N) and the volume of an appropriate aliquot should be between 100 to 200 cc., it was found more convenient and accurate to measure out the reactants separately in each flask and titrate the entire contents directly with the standard iodine. The normality of the iodine and thiosulfate solutions was changed from 0.01 to 0.001 N to meet the requirements of each experiment. They were carefully restandardized against each other just before starting a run. In Runs 25, 26 and 27 it was found that the titer of the very dilute thiosulfate solutions changed slightly during the two and one-half day period of observation, and the initial value for a was taken as the mean value, since it is reasonable to suppose that the same change was occurring in the reaction flask as in the absence of bromo-acetate.

The sodium bromo-acetate solutions for each run were made by weighing into a volumetric flask an appropriate amount of Kahlbaum's bromoacetic acid, kept over phosphorus pentoxide. Boiled water was added and the contents neutralized with 0.2 N sodium hydroxide to a faint pink color with phenolphthalein. This procedure gives a double check upon

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[7] (a) La Mer and Mason, THIS JOURNAL, 49,410 (1927), also p. 363; (b) La Mer and Cook, *ibid.*, 51,2522 (1929); La Mer and Goldman, 51,2632 (1929); (c) Gronwall, La Mer and Sandved, *Physik. Z.*, 29,358 (1928); and reference 5 (c) for a general account.

[8] Kappana, J. Indian Chem. *Soc.*, **6**, 45 (1929); also 5,293 (1928) for chloro-acetate.

TABLE I

REACTION VELOCITY DATA ON THE BIMOLECULAR REACTION $BrCH_2COONa + Na_2S_2O_3$ AT HIGH DILUTION

Temp., 25°; initial concentrations of reactants of equal normality in all cases.

Run 25. a = b = 0.001 N

50.03 cc. of 0 002 N sodium thiosulfate + 50.03 cc. of 0.002 N sodium bromo-acetate in each flask. Reaction stopped in each flask by addition of excess of dilute I_2 solution (No. 8), and back titrated with thiosulfate of approximately 0.002 N concentration. Initial titer in terms of I_2 solution No. 8 = 99.21 cc., the average of six determinations carried out over the period of two and one-half days for which the reaction was followed.

Flask no	Elapsed time, minutes	I_2 No. 8 used, cc.	$\frac{x}{a-x}$	$\frac{1}{at} \times \frac{x}{a-x} = k$	
1	2036	59.89	0 6565	0.3224	Av. k = 0.317 ± 0.003
2	2065	60.00	.6535	.3164	Log $k-1$ = 0.501
3	2133	59.03	.6807	.3191	μ = 0.0500
4	2271	57.97	.7114	.3132	
5	3318	48.56	1.0430	.3143	

Run 26. a = b = 0.0006666 N

Same as Run 25 except for addition of 50.03 cc. of boiled water to each flask.

Flask no	Elapsed time, minutes	I_2 No. 8 used, cc.	$\frac{x}{a-x}$	$\frac{1}{at} \times \frac{x}{a-x} = k$	
1	2062	69.89	0.4195	0.3051	Av. k = 0.3040 ± 0.0008
2	2066	70.03	.4167	.3027	Log $k-1$ = 0.483
3	2320	67.50	.4698	.3038	μ = 0.04082
4	3350	59.00	.6815	.3051	
5	3511	57.96	.7117	.3031	

Run 27. a = b = 0.00050 N

Same as Run 25 except for addition of 100.06 cc. of boiled water to each flask.

Flask no	Elapsed time, minutes	I_2 No. 8 used, cc.	$\frac{x}{a-x}$	$\frac{1}{at} \times \frac{x}{a-x} = k$	
1	2112	75.58	0.3127	0.2962	Av. k = 0.2981
2	3356	66.02	.5027	.2996	Log $k-1$ = 0.474
3	3559	64.80	.5310	.2984	μ = 0.03536

TABLE II

SUMMARY OF DATA FOR THE BIMOLECULAR REACTION $BrCH_2COO^- + S_2O_3^{--}$ AT HIGH DILUTION IN THE PRESENCE OF SODIUM ION. INITIAL CONCENTRATIONS OF BOTH REACTANTS OF IDENTICAL NORMALITY

No.	Normality	No of titrns in eachrun	$\sqrt{\mu}$	$k = \frac{1}{at}\left(\frac{x}{a-x}\right)$	Average log k − 1	Observer
27	0.000500	3 (S)[a]	0 0354	0.298 ± 0.001	0.474	V. K. L.
26	,000666	5 (S)	.0408	,3040 ± .0008	.483	V. K. L.
25	.001000	5 (S)	.0500	.317 ± .003	.501	V. K. L.
22	,001666	5 (S)	.0645	.325 ± .004	.512 (?)	R. W. F.
21	002500	4 (S)	.0791	.355 ± .004	.549	R. W. F.
20	.002500	5 (S)	.0791	.353 ± .002		R. W. F.
23	,005	6 (al)[a]	.1118	.385 ± .008	.586	R. W. F.
19	.005	6 (al)	.1118	.383 ± .007		
6	.005	5 (al)	.1118	.387 ± .003		R. W. F.
4	.005	3 (al)	.1118	.384 ± .002		and V. K. L.
2	.01	5 (al)	.1581	.4461 ± .0005	.649	R. W. F. and
5	.01	3 (al)	.1581	.445 ± .003		V. K. L.

[a] (al) means that aliquots were removed at definite time intervals and titrated; (S) means that each titration was made using the entire contents of flask set up as *a* separate experiment.

the concentration of bromo-acetate. Unless the weight of bromo-acetic acid and the alkali necessary to neutralize agreed to 0.1%, the mixture was made up again. Carefully performed experiments showed that the titration value of the acid was exactly that given by the formula. The purity was further tested by mixing 25 cc. of approximately 0.1 N bromo-acetic acid, neutralizing and then adding 25 cc. of 0.3020 N thiosulfate. Under these conditions the reaction is complete in twenty-four hours. The ratios of the equivalents of thiosulfate consumed to equivalents of sodium hydroxide to titrate the acid in five experiments were 0.997, 1.014, 1.000, 1.007 and 0.957, or an average of 1.005 (calcd., 1.000).

We emphasize the matter of purity since our first preparation of bromo-acetic acid, furnished by a well-known manufacturer, contained only 90% of the theoretical amount of replaceable bromine although the sodium hydroxide titration was almost 100%.

Moisture was in some way present when the batch was bottled and slow hydrolysis to glycolic acid occurred on storage. Although this hydrolytic reaction is very slow in neutral solution and does not affect our results, it is sufficiently rapid in acid solutions that one cannot make up stock solutions of bromo-acetic acid as is customary in kinetic technique and expect to use them over any considerable period of time without obtaining erroneous results.

The chief source of error seems to reside in the determination of the starch–iodide end-point. Titrations were made rapidly to avoid oxygen error, which should be slight in neutral solution. The effect of access of air during the course of the reaction deserves further study.

Detailed data are given only for the extremely dilute experiments. The probable errors are the arithmetic mean of the individual k values. All volumetric glassware was calibrated and the two stop watches when used over a period of twenty-four hours were checked against jeweler's time.

Discussion

The data of Table II are plotted as crosses in Fig. 1, the upper curve being plotted to a scale to take in Krapivin's data (circles), while the lower curve emphasizes the data in dilute solution.

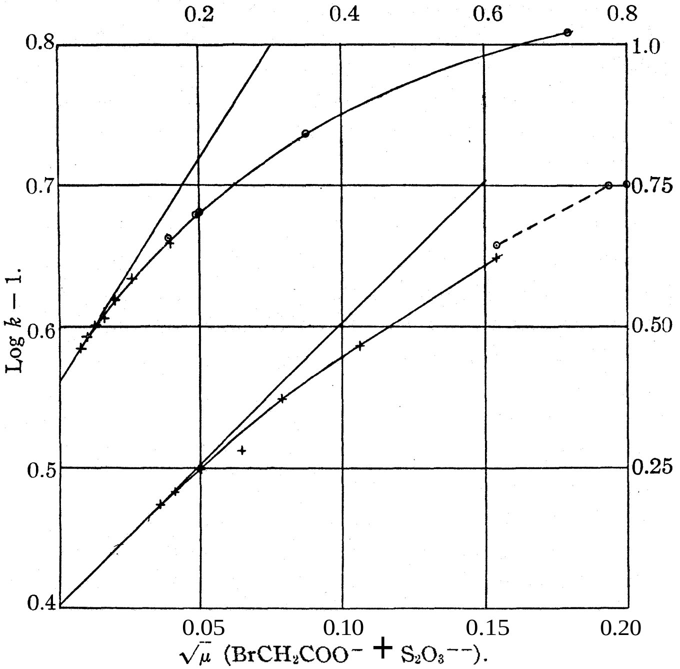
Introducing the Debye–Hückel limiting law, $\log_{10} f_i = -0.50 Z_i^2 \sqrt{\mu}$ in Equation 2, one gets

$$\log k_{\text{obs.}} = \log k_0 + Z_A Z_B \sqrt{\mu} \tag{4}$$

so that on plotting $\log k_{\text{obs.}}$ against the square root of the ionic strength, the data approach a straight line having a slope $Z_A Z_B = (-2)(-1) = +2$, with an intercept leading to a value of $\log k_0 = 0.42$ or $k_0 = 0.263$.

Our results when combined with those of Krapivin show clearly that although the slope in the region 0.35μ is only one-fourth that predicted by (4), the slope of the experimental curve continuously approaches and finally reaches the limiting value at $\mu \leqq 0.0025$ or $\sqrt{\mu}$ 6 0.05. The manner of approach is also what would be expected from the equation containing the factor of ion size in the first approximation of the Poisson–Boltzmann equation (ref. 7).

The data lend no support whatsoever to the theory of Soper,[9] that the theoretical slope should be two-thirds the value Z_AZ_B. Soper's theory[9] is not only unsound from both a thermodynamic and kinetic point of view, but in developing it the author is obliged to ignore all of the accurate solubility data supporting the Debye theory that have accumulated. The apparent agreement with the two-thirds slope which he obtains in many cases is fortuitous and results from a misunderstanding of the range of applicability of the limiting law. Kappana has also obtained data at concentrations as low as 0.0025μ. His data are sensibly parallel to ours; however, he draws a Debye limiting slope through his data at 30° up to 0.015μ, followed at this point by an abrupt change in slope to a value approximately two-thirds of the theoretical. On plotting his data at GO" we find that the transition is not abrupt but as smooth as the accuracy



⊙, Krapivin; +, La Mer.

Fig. 1.

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[9] Soper, J. Phys. Chem., 31, 1790 (1927); **32**, 67 (1928).

of the data warrant. We feel confident that some of the data at 30° must be in error.

It is of interest to note that in Krapivin's data at 0.01 N the addition of 0.01 N sodium bromide, iodide or nitrate produced identical effects, as did the further addition of 0.01 *N* bromo-acetate, *i. e.*, k increased from 0.455 to 0.502–0.505. This is in agreement with the principle of specific interaction, (see ref. 7b). On the other hand, addition of 0.01 N sodium thiosulfate gave a value of k = 0.504, while 0.01 N sodium sulfate increased *k* to 0.516, even though the ionic strength is the same as in the presence of sodium thiosulfate.

Our experiments are being continued from the standpoint of specific salt effects and the effect of the relative position of the charge and the bromine atom upon the velocity.

The assistance given by Mr. R. W. Fessenden is gratefully acknowledged.

Summary and Conclusions

The velocity data of the reaction $BrCH_2COO^- + S_2O_3{}^{--} \longrightarrow S_2O_3$-$CH_2COO^{--} + Br^-$ studied by Krapivin for the sodium salts at moderate dilutions have been extended from 0.01 N to 0.0005 N. The data strongly support Bronsted's theory of reaction velocity. In the presence of sodium ions the limiting slope predicted from the Debye theory holds from 0.001 N (0.0025~) down to the lowest concentration studied. At higher concentrations the slope falls off, reaching a value of one-fourth the theoretical value at 0.35~. The experiments are being continued.

NEW YORK, N. Y.

NOTES

A Simple Laboratory Vacuum Regulator.—Among various methods of maintaining a constant temperature in the range from room temperature to nearly red heat, the vapor-bath with boiling liquid under constant, automatically controlled, reduced pressure is perhaps the most convenient and satisfactory. The device described in this note for controlling the degree of vacuum and thus the temperature is not new in principle, but its simplicity and utility make it available to any chemical laboratory. A device based upon similar principles has recently been described.[1] The chief difference between the two devices consists in the use of a glass stopcock in the present instance instead of the combination of a rubber stopper and capillary tube to control the ingress of air.

The essential features of the apparatus are shown in Fig. 1. The mercury in the manometer AA' is adjusted by means of the leveling bottle F to such a position that when contact is broken with the platinum wire sealed into the closed arm A, the height h corresponds to the degree of

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[1] S. P. Miller and P. V. McKinney, *Ind. Eng. Chem.*, **20**, 552 (1928).

vacuum desired. Upon closing the electrical switch S, current flows from a 6-volt storage battery through the magnet coils of an ordinary door-bell buzzer, the terminals of which are connected directly to the binding posts so that the vibrator operates like the armature of a relay. The extended armature is attached at right angles to an extension of the stopcock handle in such a way that magnetization of the coils closes the stopcock C, allowing gas to be withdrawn from the condenser E and boiling tube G by means of the service vacuum or any other suitable source of suction. When the pressure in the system falls below the height h, the electrical circuit is broken, the armature is released and the stopcock opens by spring action of the relay. The influx of the air then increases the pressure until the electrical circuit is again closed, when the cycle is repeated. The manometer AA' is constructed of two wide tubes connected by a narrow tube to minimize surges.

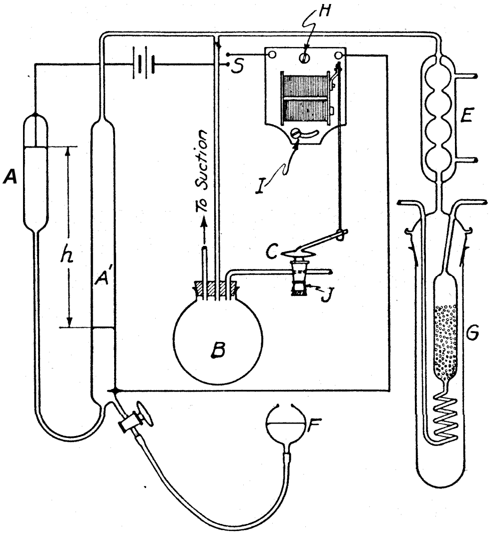

Fig. 1.

An essential feature of the automatically operated stopcock is the attachment of a short glass tube J to the small end of the stopcock barrel with de Khotinsky cement. This tube is slightly tapered and is fitted with a small cork which presses against the end of the stopcock plug to prevent the latter from settling tightly into the barrel. The stopcock is lubricated thoroughly with vaseline or a light stopcock grease. The stopcock handle may easily be extended by sealing a piece of 3-mm. diameter glass rod or tubing to it with de Khotinsky cement. A 3- or 4-liter flask B in the system serves as capacity to minimize surges. The pressure as observed on an open manometer attached to the system was constant to within less than 1 mm. of mercury at all pressures ranging from slightly less than atmospheric down to 1 cm. of mercury.

A slight adjustment of the degree of opening of the stopcock C is required for different pressures. This is accomplished by moving the relay about the screw H until the proper position with respect to the stopcock is found and then securing it in position by means of the screw I. The bore of the stopcock should be small, 1 mm. or less, so that only a slight movement entirely opens or closes it.

This device has been used continuously day and night for several months, interrupting the operation only over week ends, with only a very occasional failure, which has invariably been due to the battery running down. This device may readily be adapted to the control of vacuum distillations and other work in which a constant vacuum is desired.

Bureau of Chemistry and Soils
Fertilizer and Fixed Nitrogen Investigations
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Automatic Cut-off Device for a Gas Fired Laboratory Mercury Still.— The distillation of mercury is an operation that is usually carried out in connection with other work and the still should therefore be so designed as to require the minimum of attention. The type of glass still described by Dennis,[1] with a ring type gas burner, gives excellent results but has the disadvantage that if care is not exercised to shut off the flame when the mercury gets low in the boiler, destruction of the still results. The sketch shows diagrammatically an automatic cut-off device which enables the operator to start the still and, except for an occasional filling, then go about other business and forget that it is going.

The still itself is the usual vacuum type, consisting of a boiling vessel M and condenser L, with a 2-mm. bore capillary tube outlet of slightly greater length than the barometric column. Drops of mercury falling from the condenser into the capillary tube capture threads of gas ahead of them and thus maintain the high vacuum in the still by Sprengel pump action.[2] The mercury to be distilled is poured into the open tube A and flows through B into the still-head M. The flow stops when the difference between the

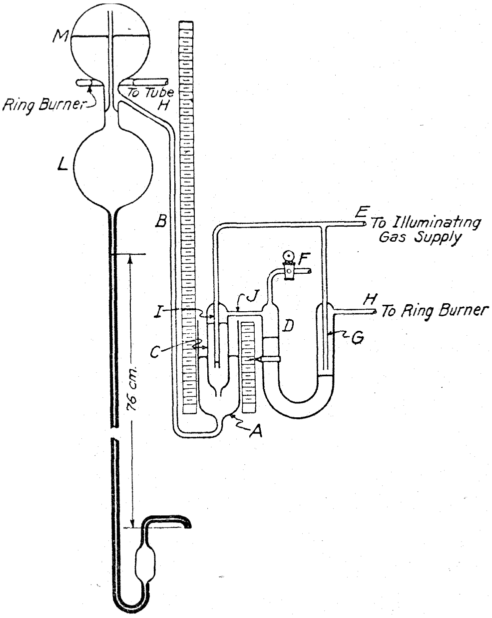

Fig. 1.

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[1] **Dennis, "Gas Analysis," The Macmillan Company, New York, 1913, pp. 119–120.**

[2] **J. Wetzel,** *Chem.-Ztg.*, **32, 1228 (1908).**

mercury levels in the still head and in **A** is equal to the prevailing barometric pressure less any slight pressure in the still. This difference in levels is maintained as the mercury distils, the level in A falling at the same rate as that in the still-head. Advantage is taken of this fact to operate the automatic cut-off device.

To start the still a slight suction is applied at F to displace the mercury in D, thus unsealing the tube G. The stopcock F is then closed so as to maintain this condition. Gas may now flow through EGH to the ring burner. The gas pressure is also communicated to I, which is immersed in the mercury in the filling tube A. As distillation proceeds, the mercury levels in M, A, C and I gradually fall until the effective seal on the tube I becomes less than that of the gas pressure within I. Gas then escapes through the mercury seal into CJD. The mercury in the U-tube is thus displaced so as to seal the open end of tube G and stop the gas flow to the burner. The tube C is extended below the open end of I sufficiently to prevent gas bubbling out through the mercury in A when the still-head cools.

The entire cut-off device is mounted to the frame carrying the still by means of a clamp (not shown) and is connected through H to the ring burner and through E to the gas supply by means of rubber tubing. The device may therefore be moved up or down to vary the depth of immersion of the tube C in the mercury in A. The depth of immersion is so adjusted that sufficient mercury remains in the still-head at the time of cut-off to cover the glass surface exposed to the flame. The level of the mercury in the still will, with a given setting of the device, vary with the mercury vapor pressure in the still-head and with the barometric pressure. The former may be held constant through the use of a constant pressure gasometer or other device to insure approximately the same rate of vaporization in the still. The latter may be corrected for if necessary by adjusting the depth of immersion of C. This may be facilitated by the use of the scale and pointer arrangement shown in the sketch. The required depth of immersion is first determined by actual operation. The still is partly filled with mercury and started with the device immersed to its full extent. When the mercury level in M reaches the cut-off position, the level of mercury in A is marked and the cut-off device slowly raised until cut-off occurs. The pointer is then fastened rigidly to D so as to coincide with the mark on A. A millimeter scale carrying the notations **720** to 780 mm. to include the normal range of barometric pressures is then mounted on A so that the pointer indicates the barometric pressure at the time of adjustment. Thereafter, in order to have the cut-off occur at the same position in M, it is only necessary to raise or lower the device until the pointer indicates the prevailing atmospheric pressure. A second scale may be attached from which the barometric pressure may be read utilizing the mercury levels in the still-head and filling tube before starting the still. This latter method has the added advantage that any slight pressure in the still is automatically compensated for.

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Adaptation of the Diphenylcarbazide Test for Mercury to the Scheme of Qualitative Analysis.—The diphenylcarbazide test for mercury is very delicate, detecting 0.0005 mg. per 2 cc., but its use so far has been restricted to practically neutral solutions.[1]

However, in the confirmation of mercury, both in Group I and in Group II, the solutions are decidedly acid. It has been found that by adding an excess of solid sodium carbonate to such solutions, the presence of considerably less than 0.1 mg. of mercury per cc. can be detected very readily. The procedure outlined below has been used for the past two years with marked success in qualitative analysis courses in this University.

The mercury precipitate in Group I is dissolved in aqua regia, that of Group II is dissolved in hydrochloric acid and sodium chlorate. In either case the solution is evaporated to a volume of about 1 cc., placed in a test-tube and diluted with 5 to 6 cc. of water. Four to eight drops of a saturated alcoholic solution of diphenylcarbazide is added and a large excess of solid sodium carbonate is gradually dropped into the solution. When mercury is present, the foam produced on neutralization assumes a blue tinge, and after the addition of an excess of carbonate the entire solution turns blue.

At the conclusion of the experiment the solution should either be blue or orange to pink in color. If the solution remains colorless, it indicates that the diphenylcarbazide solution has deteriorated.

Freshly prepared diphenylcarbazide solution is colorless, but soon develops a pink to red color. This color does not seem to affect its use for the test. However, on standing for several weeks it finally fails to give a blue color in the presence of mercuric salts. Aqua regia does not interfere provided the test is completed soon after the addition of the diphenylcarbazide solution. If the test solution containing aqua regia is allowed to stand for some hours after the addition of diphenylcarbazide, it will fail to develop any color when an excess of sodium carbonate is added.

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[1] Kolthoff, *Chem. Weekblad*, 21, 20 (1924); Stock and Pohland, *Z. angew.* **Chem.,** 39,791 (1926).

Neither sodium acetate nor sodium bicarbonate can be successfully substituted for the sodium carbonate in this test.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE MERCURATION OF HEMIMELLITIC ACID

BY FRANK C. WHITMORE AND R. P. PERKINS

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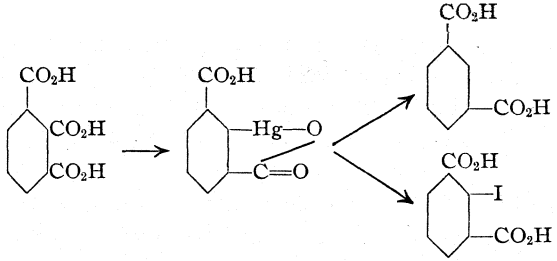
Since the treatment of 3-nitrophthalic acid with mercuric acetate[1] gives over 90% of the calculated amount of the product in which the 2-carboxyl group is replaced by mercury, it seemed desirable to study the effect of other groups on the replacement of one of two ortho carboxyl groups. The simplest case of this kind is presented by hemimellitic acid (benzene-1,2,3-tricarboxylic acid). It was found that the 2-carboxyl is replaced by mercury. No evidence of any replacement of the 1- or 3-carboxyl was found. The structure of the mercury compound was determined by replacing the mercury by hydrogen to give isophthalic acid and by iodine to give 2-iodo-isophthalic acid.



The best method of obtaining the 2-halogen isophthalic acids is undoubtedly by this procedure, starting with hemimellitic acid prepared from acenaphthene.

Experimental

Hemimellitic acid was prepared by a modification-of the method of Graebe and Leonhardt.[2] From 100 g. of naphthalic anhydride was obtained 46 g. of hemimellitic acid (44% yield), m. p. 201–203° with decomposition to form the anhydride.

A method is being developed in this Laboratory for the preparation of hemimellitic acid by the direct oxidation of acenaphthene.

A solution of 40 g. (0.2 mole) of hemimellitic anhydride in 110 cc. of 6 N sodium

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[1] Whitmore and Culhane, THIS JOURNAL, 51, 602 (1929).

[2] Graebe and Leonhardt, *Ann.*, 290, 218 (1896).

hydroxide and 170 cc. of water was treated with a solution of 43.3 g. (0.2 mole) of mercuric oxide in 40 cc. of glacial acetic acid and 70 cc. of water and refluxed for sixteen hours. At the end of that time no more carbon dioxide was evolved and the precipitate which had formed was soluble in sodium hydroxide. The product was separated by filtration, washed and dried to constant weight at 105°; weight, 70.2 g. of anhydro-2-hydroxymercuri-isophthalic acid (96% yield).

Anal. Calcd. for $C_8H_4O_4Hg$: Hg, 55.0. Found: 55.0.

Ten grams of the mercury compound was dissolved in dilute sodium hydroxide, filtered from a slight residue and refluxed for two hours with enough excess hydrochloric acid to make the solution about 6 *N* in hydrochloric acid. The isophthalic acid obtained weighed 3.6 g. (79% yield). It sublimed without melting or decomposing. The dimethyl ester prepared by means of thionyl chloride and methanol melted at 67–68°.

Ten grams of the mercury compound was powdered and dissolved in 75 cc. of 20% potassium iodide solution. To this was added 7.5 g. of iodine. After standing for one hour, the small excess of iodine was removed by concentrated sodium thiosulfate solution. The mixture was acidified and cooled. Highly twined colorless needles separated almost immediately; weight of 2-iodo-isophthalic acid, 5.9 g. (73% yield), m. p. 241.5–243°. Crystallization from water raised the melting point to 243–244°.[3] Treatment of the acid with thionyl chloride and methanol gave the dimethyl ester, m. p. 49.5–50.50°.[4]

Summary

1. Hemimellitic acid reacts with mercuric acetate with the replacement of the 2-carboxyl by mercury.

2. Treatment of this mercury compound with halogens gives the best method of preparing 2-halogenated isophthalic acids.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF HYDROCARBONS: NORMAL-BUTANE AND ISOBUTANE[1]

BY CHARLES D. HURD[2] AND L. U. SPENCE[3]

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The present investigation with *n*- and isobutane inaugurates a series of studies dealing with the behavior of individual hydrocarbons at high

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[3] The melting point of this substance is given as 236–238° by James, Kenner and Stubbings, J. *Chem. Soc.*, 117,774 (1920).

[4] *Cf*. Mayer, ***Ber.***, 44, 2301 (1911).

[1] This paper contains results obtained in an investigation on "The Non-Catalytic Thermal Decomposition of Pure Hydrocarbons and Related Compounds," listed as Project No. 18 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project No. 18.

[3] American Petroleum Institute Junior Research Fellow.

temperatures. The evidence which was obtained with n-butane points to two equations for the representation of the major part of the pyrolysis

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_4 + CH_3CH{=}CH_2$$
$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_3 + CH_2{=}CH_2$$

At 600° the first of these appears to proceed to the extent of about **55%** and the second to 40%. Dehydrogenation reactions into butene or butadiene appear to represent less than **5%** of the total. These results were obtained by exposing the hydrocarbon at 600° for thirty seconds or less by a single passage through a pyrex tube. The rate of flow was about 6 cc. per second, and about one-fifth of the butane suffered decomposition. Similar results were obtained when a temperature of 700° was used. The chief points of difference are these. The extent of the decomposition was 75% instead of 22%. Indicative of secondary reactions, the propylene–ethylene ratio changed so that ethylene was somewhat in excess. This is reasonable since propylene is known[4] to decompose more readily than ethylene, and since ethane is known to pyrolyze into ethylene.

In similar experiments isobutane differed noticeably from n-butane in giving rise to a large production of hydrogen. Except for the considerable excess of methane, which is a characteristic feature, the primary decomposition of isobutane at 600° may be represented by the equations

$$(CH_3)_3CH \longrightarrow H_2 + (CH_3)_2C{=}CH_2$$
$$(CH_3)_3CH \longrightarrow CH_4 + CH_3CH{=}CH_2$$

Since 38.5% of the unsaturated hydrocarbons (formed at 600°) is propylene **and** 50.8% is isobutylene, it would appear superficially that the first reaction takes place to the extent of **51%** and the second, **39%.** However, since the methane–propylene ratio is over 2:1, and since ethylene is present in appreciable quantities, quantities in fact which become rather formidable at 700°, it may be fortuitous that the hydrogen–*iso*butylene ratio is approximately 1:1. In the absence of evidence to the contrary, these facts may be explained by postulating that the hydrogen which was momentarily liberated failed to appear entirely as molecular hydrogen. Instead, it may have caused scission of some of the isobutylene into "methane + propylene," and also have converted part of the propylene into "methane + ethylene." In a subsequent paper we will show that at 700" isobutylene very definitely consumes large quantities of hydrogen with the consequent production of the anticipated excess of methane.

The general course of pyrolysis of isobutane is the same at 700° as at 600°, but the extent of the change was found to be considerably greater and the secondary reactions assumed greater prominence. Whereas more isobutylene than propylene was noted at 600°, the reverse was true at 700°. Small amounts of a liquid tar were formed at 700°, but in

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[4] Frey and Smith, *Ind. Eng. Chem.*, **20,950 (1928).**

quantities insufficient for identification. Experiments (unpublished data) with olefins lead us to believe that this tar formation was caused by the *iso*butylene or propylene formed in the reaction. As stated above, ethylene was formed in fair amounts at 700°.

It is believed that the results of this study may be interpreted satisfactorily by assuming an initial scission of the saturated hydrocarbons into radials. Such splitting may occur at C–C or C–H bonds. If this is the case, scission with n-butane is largely of the C–C type, division occurring at the terminal position slightly more readily than at the central position. Although rupture of the C–C bond is a large factor in the pyrolysis of isobutane, the C–H type of scission predominates, possibly because of the low attraction which the tertiary butyl radical is known to have for electrons.

Since this work on the butanes has been completed, a paper by Pease[6] has appeared which deals with the decomposition of the butanes as well as of ethane and propane. Pease approached the problem from a different point of view. His chief concern was the rate of dissociation of the various hydrocarbons, rather than the mechanism of the reaction. In his work the individual hydrocarbons which were formed in the pyrolysis were, for the most part, not identified. It was practically assumed, for example, that methane was the only saturated hydrocarbon which was formed, and no effort was made to identify the individual unsaturated hydrocarbons. It is with the latter problem in particular that this paper deals.

Two methods were developed for the analysis of the unsaturated content of the gaseous hydrocarbon mixtures which were produced. In one the olefins were converted in quantity into their bromide derivatives and then, if possible, fractionated into pure fractions or into two-component mixtures. Each such fraction was analyzed by the index of refraction method. For this work it was necessary to construct index of refraction curves for reference from synthetic mixtures of ethylene–propylene bromides, and of propylene-isobutylene bromides.

Another analytical method, better than the first, was developed. In this each of the gaseous unsaturated hydrocarbons was directly absorbed in a modified Orsat apparatus. Acetylene and methylacetylene were dissolved in alkaline potassium iodomercurate[6] solution, following which the remaining unsaturated hydrocarbons were removed in turn by sulfuric acid of progressively greater concentration. This is essentially the method suggested by Dobryanskii,[7] but critical studies were carried out

[5] Pease, This Journal, 50, 1779 (1928).

[6] Lebeau and Damiens, *Ann. chim.*, 8,221 (1917).

[7] Dobryanskii, *Neftyanoe Khozyaistvo*, 9, 565 (1925); *Chem. Zentr.*, I, *97*, 2220 (1926); *Petroleum Domain*, 565 (1925); *C. A.*, 20, 1576 (1926).

with it to adapt it to our needs. Dobryanskii suggested 63–64% sulfuric acid as the proper solvent for isobutylene; 83–84% acid for propylene; and 100–102% acid for ethylene. We obtained more satisfactory results with the acid concentrations, respectively, of 62.4, 82.5 and 100% acid which contained 8% of sulfur trioxide. We found allene to be nearly insoluble in the isobutylene pipet, but readily soluble in the propylene pipet. Although the absorption method, for obvious reasons of convenience, economy and precision, is superior to the bromide method, it must be used advisedly, since more than one hydrocarbon in a hydrocarbon mixture may be appreciably dissolved in the reagents employed.

Experimental Part

Apparatus.—A flow method was used. The gaseous hydrocarbon was passed directly from the tank through a wet test meter, then through a differential pressure flowmeter of the capillary type, was dried by calcium chloride and passed into the reaction tube. This tube was of pyrex, one inch in diameter, and was heated over 30 inches of its length in an unsegmented electric tube furnace. The furnace was supported in a vertical position to facilitate the escape of any liquid products from the heated portions. Butane was passed through the tube at a controlled rate of flow, and the effluent gases were passed through cooling coils at 0° to remove liquid products. The gaseous products were then analyzed.

Gas Analysis.—A modified Orsat gas analysis apparatus was constructed and the values for carbon dioxide, oxygen, total unsaturated hydrocarbons, hydrogen, carbon monoxide and saturated hydrocarbons were determined in the usual way. Presumably methane and isobutane are the only saturated hydrocarbons present in the mixture from isobutane. Combustion analysis is satisfactory for such a mixture. From n-butane, however, it is likely that three saturated hydrocarbons are present, methane, ethane and n-butane; combustion data give the average molecular weight of such a mixture. By assuming that ethane and ethylene are formed in equivalent amounts and that methane and propylene are also, the relative amounts of methane, ethane and butane may be estimated.

To analyze the individual unsaturated hydrocarbons, 3 pipets filled with glass tubes were incorporated in the apparatus. They were for acetylene, isobutylene and propylene[8] in turn, after which ethylene was removed with fuming sulfuric acid (8% SO_3). The acetylene reagent was made up from 500 g. of potassium iodide, 200 g. of mercuric chloride and 40 g. of sodium hydroxide, and diluted with water to one liter. The *iso*-butylene pipet contained 62.4% sulfuric acid and the propylene pipet 82.4% sulfuric acid. The ethylene reagent was prepared by adding 120 g. of sulfur trioxide to 200 cc. of 95% sulfuric acid. The sequence of the analysis is: carbon dioxide, acetylenes, *iso*-butylene, propylene, ethylene, oxygen, hydrogen and carbon monoxide, saturated hydrocarbons. In the sulfuric acid pipets the sample of gas was left in contact with the acid for two minutes, then withdrawn, and the process repeated until constant volume was attained.

With sulfuric acid of 60.7% strength, the rate of solution of diluted isobutylene (mixed with 70% air) was very slow. By changing the acid strength to 62.4%, *iso*-

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[8] Allene, butene-1 and butene-2 are also rapidly absorbed in the propylene pipet. These three gases were shown, however, to comprise less than 2% of the total gases. Butadiene, also present in traces, would be taken up in this pipet and to some extent also in the isobutylene pipet.

butylene dissolved rapidly. About twenty to thirty minutes was required for complete absorption and most of this time was taken to remove the last 2 cc. of isobutylene from the 70 cc. of air. Propylene (31% by volume, mixed with air) was not dissolved by this 62.4% acid in a total contact time of ten minutes, but pure propylene was absorbed at the slow rate of 0.03–0.08 cc. per minute of contact. Since the gases from a thermal decomposition will never produce undiluted propylene, this becomes a separation of high accuracy. No loss of ethylene could be detected in a total contact time of twelve minutes with either 62.4 or 82.4% sulfuric acid, but a solution of 84.4% acid absorbed it at a rate of about 0.02 cc. per minute. Since propylene was rapidly dissolved in 82.4% acid, this concentration was adopted. The time of complete absorption far a mixture with air (45% C_3H_6) was twenty to twenty-five minutes. Allene, $CH_2{=}C{=}CH_2$, was found to be nearly insoluble in 62.4% sulfuric acid when the allene was of 40% concentration (60% air). It was quickly absorbed by 82.4% acid, however.

In the absorption of ethylene of 75% concentration (25% air) by fuming sulfuric acid (8% SO_3), completion was reached after seven two-minute passes. The final reading was preceded by an alkaline wash. Both butanes interfere in this analysis, but since they appear to be absorbed at a constant rate, a correction may be made for this effect. A measured sample of isobutane was kept in the "ethylene pipet" for two minutes. Then it was transferred to the potassium hydroxide pipet and the volume again read. Six consecutive passes gave a mean loss of 0.71 cc. for a mean volume of 92.5 cc. With *n*-butane, the loss was about 0.6 cc. In mixtures of ethylene with butane, these values obviously depend on the residual volume of butane, but one or two two-minute passes after final absorption of the ethylene will indicate the "constant" for the experiment in question. Correction may then be made.

Refractive Indices of Synthetic Mixtures of Olefin Bromides,—Ethylene brotnide, propylene bromide and isobutylene bromide were purified by vacuum distillation. The svnthetic mixtures used for these determinations were ethylene–propylene bromides and propylene–*iso*butylene bromides. The refractive indices were determined with a water-jacketed Abbé refractometer equipped with a standardized thermometer. The results are listed in Table I.

TABLE I

REFRACTIVE INDICES OF SYNTHETIC OLEFIN BROMIDE MIXTURES

Ethylene–Propylene			Propylene–*Iso*butylene		
Per cent. by weight		n_D^{20}	Per cent. by weight		n_D^{20}
$C_2H_4Br_2$	$C_3H_6Br_2$		$C_3H_6Br_2$	$C_4H_8Br_2$	
0.00	100.00	1.5198	100.00	0.00	1.5198
9.79	90.21	1.5208	74.8	25.2	1.5165
28.90	71.10	1.5240	56.6	43.4	1.5150
44.96	55.04	1.5268	41.0	59.0	1.5143
67.80	32.20	1.5313	0.00	100.0	1.5118
89.20	10.80	1.5356			
100.00	0.00	1.5379			

Temperature Measurements.—The temperature of the reaction was measured by a chromel-alumel thermocouple which was within the reaction tube and which was protected by a thin pyrex tube. This temperature was recorded and automatically controlled by a Leeds and Northrup potentiometer type recorder-controller. The usual sensitivity of this system was ±2°, but with a carbon coating on the protecting tube there was a lag, the extreme case of which was ±8°.

Source and Purity of the Butanes.—Cylinders of the liquefied gases were purchased from the Carbide and Carbon Chemicals Corporation; high purity was claimed for them; combustion analysis showed them to be fairly pure. Analysis of n-butane gave values of 4.04 and 3.96 for n in C_nH_{2n+2}; isobutane gave values of 3.93, 3.92 and 3.97. These are all sufficiently near the theoretical value of 4.00 to be satisfactory. The n-butane contained traces of pentane and 1–2% of isobutane as impurities. *Iso*-butane contained a small amount of propane and 1–2% of n-butane as impurities.

Increase in Volume, Percentage Decomposition, Rates of Decomposition.—In the preliminary experiments the influence of the temperature and the rate of flow of the hydrocarbon into the tube was studied and the progress of the reaction was followed by analyzing the gases for total unsaturated hydrocarbons and hydrogen. The contact time was calculated by dividing the volume of the heated portion of the tube by the mean volume of gas entering and leaving the tube, this mean volume being corrected to the temperature of the tube.

The primary pyrolytic reactions of n-butane are: (1) into $C_3H_6 + CH_4$, (2) into $C_2H_4 + C_2H_6$, (3) into $C_4H_8 + H_2$. The primary changes of isobutane are: (1) into $C_3H_6 + CH_4$, (2) into *iso*-$C_4H_8 + H_2$. Assuming no secondary changes into acetylene, allene, butadiene, etc., it is evident that from 100 volumes of n- or isobutane there

TABLE II

VOLUME INCREASE OF THE BUTANES DURING PYROLYSIS

Butane	Temp., °C.	Rate of flow into tube, cc. per min.	Unsatd. hydrocarbons in exit gas, % by volume	Volume increase, % Calcd.	Obs.
n-	600	360	17.3	20.9	16 ± 3
n-	600	336	19.2	23.8	15 ± 4
n-	700	312	38.8	63.5	88 ± 5
n-	700	315	41.6	71.5	82 ± 5
iso-	600	320	20.6	26.0	17 ± 3
iso-	700	297	36.3	57.0	79 ± 4

TABLE III

RESULTS WITH *n*-BUTANE

Temp., °C.	Contact time, sec.	Rate of inflow (20°, 760 mm.), cc./min.	Analysis of effluent gas, % Unsat.	H_2	Extent of dec., %	Extent of dehydrogenation, %
400	31	300	1.3	0.9	1.3	1.0
500	27	300	1.8	1.1	1.85	1.2
600	19	360	17.3	1.8	21.0	..
600	19	336	19.2	1.0	23.8	1.1
600	22	300	13.8	1.4	16.0	1.6
			Results with Isobutane			
400	30	310	1.1	0.9	1.1	0.9
500	27	295	6.9	1.3	7.4	1.1
600	21	320	16.3	6.2	19.5	7.2
600	17	400	11.7	5.5	13.2	6.1
500	8	1000	1.4	0.5	1.5	0.5
550	8	900	5.1	1.3	5.4	1.3
550	10	720	7.0	0.4	7.5	0.5
600	9	800	9.9	2.0	11.0	2.3
650	7	920	16.2	5.8	19.4	7.2
700	6	1040	27.8	10.7	38.6	15.2

TABLE IV

DATA FOR THE PYROLYSIS OF THE BUTANES

	n-Butane				*Iso*butane			
Temperature, °C.	600	600	700	700	600	600	700	700
Entering rate of flow, cc./min.	345	430	390	350	346	395	330	400
Vol. of heated part of tube, cc.	550	550	550	550	550	500	550	360
Exit rate of flow (20°, 760 mm.); cc./min.	395	500	740	630	400	455	595	720
Hot contact time, sec.	30	24	18	20	27	26	21	12
Final vol. from 1000 cc. of orig. butane, cc.	1155	1150	1870	1820	1150	1190	1800	1790
Extent of decomp., %	22	20	75	76	22	25	70	70
	Anal. of effluent gas Percentage by volume							
Acetylenes	0.2	..	1.2	..	0.4	..	0.6	..
Isobutylene	0.6	..	2.0	..	7.2	..	11.6	..
Propylene	7.7	..	16 2	..	5.5	..	13.2	..
Ethylene	6.1	..	19.0	..	1.1	..	6.4	..
Total unsatd. gases	14.6	19.2	38.4	41.6	14.2	20.2	31.8	36.3
Hydrogen	2.0	1.0	8.5	7.8	6.8	6.2	12.7	15.2
Methane	..	..	..	..	11.3	11.0	31.3	26.3
*Iso*butane	..	..	..	..	67.9	62.8	16.6	17.0
Nitrogen	..	..	..		..	..	7.5	5.0
	Comp. of the unsatd. hydrocarbons Percentage by volume							
	Abs.[a]	Brom.[a]	Abs.	Brom.	Abs.	Brom.	Abs.	Brom.
Ethylene	40.1	32.6	49.3	46.0	7.8	..	20.1	2.5
Propylene	55.4	64.6	42.2	43.7	38.8	50.8	41.5	74.8
Butylenes	..	1.3	..	4.8	..	..	..	..
Isobutylene	3.4	..	5.3	..	50.7	46.6	36.5	19.8
Acetylenes	1.2	1.5	3.1	3.7	2.8	..	1.9	..
Acetylenes and dienes	..	..	..	..	..	2.5	..	2.9
Butadiene	..	..	..	1.6	..	..	..	..

[a] The abbreviation Abs. indicates that the unsaturated hydrocarbons were analyzed by the absorption method; the abbreviation Brom. signifies the bromine method of analysis.

	Vol. of prods. formed per liter of butane taken Cubic centimeters							
Ethylene	71	..	356	..	13	..	115	..
Propylene	89	..	304	..	63	..	238	..
Butenes and butadiene	7	..	39	..	..	..	..	..
Isobutylene	..	..	..	..	83	..	209	..
Acetylene	2	..	22	..	5	..	11	..
Total unsatd. gases	..	222	..	760	..	240	..	650
Hydrogen	23	12	159	142	78	74	228	272
Methane	80	..	312	..	130	131	563	468
Ethane	65	..	370	..	..	..	..	..
Methane + ethane	..	128	..	686	..	..	..	..
Undec. butanes	780	798	250	241	780	750	299	302

should be produced ((100 − P) volumes of C_4H_{10}) + (P volumes of C_2H_6, CH_4 and H_2) + (P volumes of olefins). The sum of these three quantities represents the total new volume, or V. Thus

$$V = (100 - P) + P + P = 100 + P$$

From this the percentage by volume of olefins, U, in the escaping gas is related to the percentage decomposition, P, of the butane as follows

$$U = \frac{100P}{100 + P} \qquad P = \frac{100U}{100 - U}$$

Experimentally it was determined that the agreement with both butanes was fair at 600°, but the rather wide divergence at 700" indicated considerable secondary decomposition. In these measurements of volume increase, the volumes were measured roughly in bottles of 8-liter capacity and calibrated in 100-cc. divisions. Table II lists a few of the results.

The decomposition of n-butane showed a rapid increase in rate between 500 and 600°. The rates of decomposition at 600" of n- and of isobutane are of the same order of magnitude, as is apparent from Table III. The data also show strikingly the limited extent of the dehydrogenation reaction with n-butane and the importance of it with isobutane, which at 600° is seen to represent 36–47% of the total reaction.

The more representative data for two representative runs at 600° and for two at 700° with n-butane and the same for isobutane are collected in Table IV. It will be noticed that the unsaturated hydrocarbons in one 600" experiment and in one 700° experiment for each of the butanes were determined directly by absorption methods. In the other four runs the olefins were estimated by the bromine method. These two methods are seen to check each other fairly well with n-butane, but not with isobutane. This is due to the more complex olefin mixture in the latter case. For the simple olefins, the absorption method is considered much more trustworthy, but the bromine method was especially useful in the search for butadiene, allene and methylacetylene. From isobutane it is apparent that allene and butadiene either were not present or were present in very limited amounts, since the acetylene values by the absorption method were of the same order of magnitude as the "acetylene and diene" values by the bromine method.

Data for the Bromine Method of Analysis Referred to in Table IV.—From n-butane at 60° the weight of bromides which were fractionated with a Vigreux column was 148 g. The percentage composition of each fraction is taken from the index of refraction curves.

Boiling range mm.	Boiling range °C.	Weight, g.	n_D^{20}	Composition by weight, % $C_2H_4Br_2$	$C_3H_6Br_2$	$C_4H_8Br_2$
25	4243	92.8	1.5259	40	60	..
23	4345	41.7	1.5220	17	**83**	..
23	47–57	4.97	1.5172	..	50	50
22	107–125	3.32	....			
Residue		5.0	....	Some butadiene tetrabromide		

Loss, 1.9 g., or 1.2%

A total of 43 liters (20°, 760 mm.) of n-butane in the 700° experiment yielded 219 g. of bromides, which, twice fractionated, gave these results.

Boiling range mm.	°C.	Weight, g.	n^{20}_D	Composition by weight, % $C_2H_4Br_2$	$C_3H_6Br_2$	$C_4H_8Br_2$
24	4043.5	85.0	1.5295	60	40	...
22	4143	95.7	1.5260	40	60	...
21	4344	2.04	1.5183	..	80	20
7	2845	8.71	1.5220	..	..	100 ?
6	56–100	5.12	1.5542	..	..	...
4	104–120	7.24	....	Some butadiene tetrabromide		
Residue		7.05	....	Much butadiene tetrabromide		
		Loss, 5 07				

Butadiene tetrabromide was present in quantity in the 104–120" (4 mm.) fraction and the residue. After several recrystallizations from alcohol, there was separated 3 g. of the material which melted at 115–115.5".

Anal. Calcd. for $C_4H_6Br_4$: Br, 85.4. Found: Br, 86.0, 85.9.

The bromides from isobutane at 600° weighed 107 g., and gave these data.

Boiling range mm.	°C.	Weight, g.	n^{20}_D	Apparent composition[a] (% by wt.) $C_3H_6Br_2$	*iso*-$C_4H_8Br_2$
38	54.5-55.0	4.15	1.5175	85	15
32–28	52.3-51.0	40.04	1.5162	72	28
27	51.0-52.0	26.38	1.5144	44	56
27	52.0-52.5	8.09	1.5123	4	96
2	63.0-69.0	11.92	1.5650	Almost pure $CH_3CBr(CH_2Br)_2$	
Residue		4.15	....		

[a] The presence of ethylene bromide is masked by the isobutylene bromide in the n_D values.

The residue represents the tetrabromide fraction (acetylenes and dienes) but it was too small to investigate satisfactorily. The fraction, b. p. (2 mm.) 63–69', was shown to be almost pure tribromo-*iso*butane, formed by the action of isobutylene and bromine water. This material, therefore, represents isobutylene. It was united with similar material from the 700° experiment and was purified by vacuum fractionation. A fraction which weighed **13** g. had these properties: b. p. (3 mm.) 69–70'; d^{20}_4 2.1887; d^{25}_4 2.1803; n^{20}_D 1.5669.

Anal.[9] Subs. 0.1915, 0.2005: *N*/15 $AgNO_3$ soln., 29.25, 30.55 cc. Calcd. for $C_4H_7Br_3$: Br, 81.35. Found: Br, 81.4, 81.2.

The weight of olefin bromides formed from 46.72 liters of *iso*butane at 700' was 212 g. A very small quantity of butadiene tetrabromide, m. p. 113–115°, was isolated from the fraction, b. p. (4 mm.) 91–110°, and the residue.

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[9] Analysis was by the method of Drogin and Rosanoff, THIS JOURNAL, 38, 713 (1916).

Boiling range mm.	°C.	Weight, g.	n_D^{20}	Apparent composition (% by wt.) $C_2H_4Br_2$	$C_3H_6Br_2$	*iso*-$C_4H_8Br_2$
25	45–46	71.6	1.5204	6	94	..
24	45–46	45.7	1.5197	..	100	..
22	4648	38.2	1.5160	..	70	30
3	28-60	4.0	....	..	...	..
2	62–72	31.7	1.5667	Entirely tribromo-*iso*butane		
4	91–110	4.4	....			
Residue		5.6	....			

Summary

Two concurrent reactions predominated in the pyrolysis of n-butane at 600°, namely, that into propylene and methane, and that into ethylene and ethane. The first of these reactions was slightly favored. Also, two major reactions occurred in the pyrolysis of isobutane at 600°, the formation of isobutylene and hydrogen, and to a lesser extent the formation of propylene and methane. An explanation is suggested for the observation that considerably more methane was formed from *iso*butane than would be accounted for by the latter reaction. These reactions were still the major ones with n- and *iso*butane at 700°, but not in the same proportions. Secondary reactions of importance were also encountered and studied.

Two methods were developed for the estimation of the individual unsaturated hydrocarbons in the gaseous mixtures which were encountered. One method, with limitations which were noted, consisted in determining the refractive index of the various bromide fractions (obtained from the olefins) and referring the values to index of refraction curves for similar synthetic mixtures. In the second analytical method, which is superior in most respects, the individual unsaturated hydrocarbons were selectively absorbed from the mixture by reagents in a modified Orsat apparatus. The various conditions for the analysis have been indicated.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE MERCURATION OF NAPHTHOIC ACIDS. I. 1-NAPHTHOIC ACID

BY PRANK C. WHITMORE AND ARTHUR L. FOX

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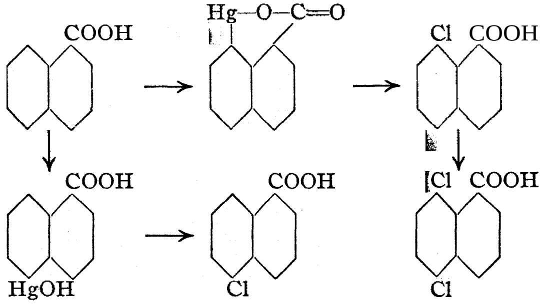
The present paper is a continuation of the studies on mercuration and the preparation of organic mercury compounds of higher molecular weight which have been carried on in this Laboratory during the past ten years.

1-Naphthoic acid reacts readily with mercuric acetate to give a mixture of mercurated acids substituted in the 5- and 8-positions. The structure of the mercurated products was determined by replacement of the mercury by chlorine. The structure of the 8-chloro-1-naphthoic acid was confirmed by chlorination to give 5,8-dichloro-1-naphthoic acid.



A considerable by-product of the mercuration was an alkali-insoluble organic mercury compound formed with the loss of carbon dioxide. This product contained two mercury atoms probably in the 1,5-positions.

In the course of the study anhydro-8-hydroxymercuri-1-naphthoic acid obtained from naphthalic acid was changed to the 8-chloro- and the 8-bromo acids. This is the best available way to obtain the 8-halogen-1-naphthoic acids in quantity and in a high degree of purity.

Experimental Part

Preparation of **1-Naphthoic** Acid.—Several methods were studied. Fusion of sodium 1-naphthalene sulfonate with sodium formate gave a 6 to 8% yield. Heating the same materials in kerosene gave none of the desired acid. The use of the calcium salt in the fusion with sodium formate gave a 9% yield. Passage of the vapors of 1-bromonaphthalene over heated potassium ferrocyanide gave no naphthonitrile. Treatment of 1-naphthylamine by the Sandmeyer reaction gave none of the nitrile.

The best methods of preparing 1-naphthoic acid were found to be through its nitrile formed by fusion of sodium 1-naphthalene sulfonate with sodium cyanide and from 1-bromonaphthalene through the Grignard reagent and treatment with carbon dioxide.

Sodium 1-naphthalene sulfonate was prepared by sulfonating naphthalene with concentrated sulfuric acid at 40–50°, neutralization with calcium hydroxide, treatment with sodium carbonate solution, removal of calcium carbonate by filtration and evaporation of the filtrate to crystallization.

A mixture of 920 g. (4 moles) of dry sodium 1-naphthalene sulfonate and 196 g. (4 moles) of sodium cyanide was prepared by grinding the materials together in a meat grinder and passing the mixture several times through a sieve. The retort used was a 3-inch iron pipe about 3 feet long with one end closed by a cap and the other provided with a flange fitted to another flange bearing a half-inch bent pipe about 6 inches long. The large pipe was placed on end and a stick about $^3/_4$ inch in diameter was placed in it. The mixture for fusion was then filled into the pipe to within about 6 inches of the top. A hard asbestos gasket was stuck to the flange with sodium silicate solution. The iron pipe with the stick at the top was then placed horizontally in a gas-heated combustion furnace. The stick was withdrawn, leaving a free space above the whole length of the mixture. The other flange was bolted on and the small pipe was connected with a flask set in an air-bath. This flask was connected with a vertical condenser and five wash bottles containing benzene. The end of the system was connected with a water pump. The combustion furnace was turned on full force. The nitrile started to distil almost immediately. Several runs were made without emptying the receiving system. The crude cyanide was separated from a small amount of water and distilled. The main fraction boiled at 285–300°. A considerable amount was recovered from the benzene wash bottles.

The 1-naphthonitrile was hydrolyzed by the method of Kamm,[1] refluxing 50 g. of nitrile with 100 cc. each of sulfuric acid, acetic acid and water for four hours. Treatment of the precipitated product with ammonium hydroxide dissolved all except 3 g. The filtrate from this material was acidified with hydrochloric acid and the solid collected on a filter; m. p. 145–155°; wt., 55 g. (98% yield). With considerable difficulty the acid was purified to its true melting point of 161° by crystallization from dilute acetic acid, dilute ethyl alcohol or xylene. The best method of purification was by esterification and vacuum distillation of the ethyl ester with subsequent hydrolysis; boiling point of ethyl 1-naphthoate, 183–186° (20 mm.).

The Grignard reagent prepared from 103.5 g. (0.5 mole) of 1-bromonaphthalene and 12 g. (0.5 g. atom) of magnesium in 1.5 Liters of dry ether was treated under vigorous stirring with dry carbon dioxide gas. The Grignard addition product adhered to the walls of the flask as a green tar. The ether was decanted for use in another run. The tar was treated with dilute hydrochloric acid with the formation of crude 1-naphthoic acid. It was dissolved in ammonium hydroxide, boiled with dccolorizing carbon and fuller's earth and filtered. The filtrate was allowed to stand for twenty-four hours to allow a small amount of a very troublesome tar to separate. After the addition of a little fuller's earth and filtration, the light green or straw-colored solution was acidified with hydrochloric acid. Pure white 1-naphthoic acid separated; m. p. 148–152°; wt., 40–45 g. (46–52% yield).

Mercuration of 1-Naphthoic Acid.—The mercuration of this acid took place with extreme ease but the products were most unmanageable. A total of 1357 g. of 1-naphthoic acid was mercurated in 39 experiments with a systematic variation of solvent,

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[1] Private communication.

concentration, temperature and time of heating. The results of all the experiments were roughly similar. Only one will be given here.

A solution of 172 g. (1 mole) of 1-naphthoic acid in 210 cc. of 5 N sodium hydroxide and 2 liters of water was placed in a flask provided with a dropping funnel, a mercury seal stirrer and a reflux condenser connected with weighed potassium hydroxide traps to catch the carbon dioxide evolved. The stirrer was started and the mixture was heated to boiling. A solution of 318 g. (1 mole) of mercuric acetate in 1.5 liters of water and 60 cc. of acetic acid was added gradually. A white granular precipitate formed at once. Gas was evolved slowly. The mixture was rcfluxed for forty-four hours. The apparatus was then swept out with air free from carbon dioxide. The carbon dioxide absorbed by the potassium hydroxide was 4.98 g. The cream-colored precipitate in the flask was treated with 280 cc. of 5 N sodium hydroxide. Part of it dissolved and the rest turned black, due to the presence of mercurous compounds. The insoluble portion weighed 80 g. The alkaline filtrate was saturated with carbon dioxide. The precipitate formed was filtered and redissolved in sodium hydroxide solution. It was again precipitated by carbon dioxide; wt., 240 g. The filtrate from the mercurated product gave 34 g. of unchanged 1-naphthoic acid when acidified with hydrochloric acid.

As will be shown below the chief product consisted of hydroxymercuri-1-naphthoic acids having the mercury in the 5- and 8-positions. The alkali-insoluble product was mainly a dimercurated naphthalene.

The above mercuration experiment can be summarized as follows

1-Naphthoic acid recovered unchanged, g.	34
1-Naphthoic acid equivalent to 240 g. of Hg compound, g.	110.5
1-Naphthoic acid equivalent to 80 g. of Hg_2 compound, g.	24.5
1-Naphthoic acid not accounted for, g.	3
1-Naphthoic acid started with, g.	172

The amount of mercurous compound formed by oxidation–reduction reactions was not determined. The amount of carbon dioxide recovered was only 80% of the amount calculated from the amount of alkali-insoluble dimercurated product obtained.

Purification and Identification of Mercury Compounds Obtained from 1-Naphthoic Acid.—Literally hundreds of experiments were carried out to separate the mixture of hydroxymercuri-I-naphthoic acids into pure chemical individuals. Many fractionations were obtained by the use of a variety of solvents. In almost all cases fractions were obtained which contained 44 to 55% of mercury (calcd. for anhydro-hydroxymercuri-1-naphthoic acid, Hg, 54.05).

It was finally decided to convert the mixture of mercury compounds to a mixture of halogenated 1-naphthoic acids and to separate these.

Attempts to obtain iodonaphthoic acids by treatment with a chloroform solution of iodine gave only tarry products.

Replacement by bromine was more successful. A solution of 60 g. of the mixed hydroxymercuri-1-naphthoic acids in 60 cc. of 5 N sodium hydroxide and 300 cc. of water was heated with decolorizing carbon, filtered and barely acidified with hydrochloric acid. The chloromercuri compound was separated and suspended in 800 cc. of acetic acid and treated with 28 g. of bromine dissolved in sodium bromide solution. As the bromine solution was added, the color disappeared until the last was added when the red color remained. On boiling, the solution became clear but the color of bromine persisted. This was removed by treatment with a little sodium bisulfite. After boiling with decolorizing carbon and filtering, the solution was cooled. Crystals were obtained which melted at 226–230°. After several crystallizations from glacial acetic acid, the product melted at 248–250°. It was 5-bromo-1-naphthoic acid.[2] The mother liquors gave more of this acid and another acid which was not successfully purified.

Although the replacement of mercury by chlorine is not generally used in determinations of structure, it was decided to attempt it in this case.

An alkaline solution of 132.5 g. of the mixed hydroxymercuri-1-naphthoic acids was treated with 20 g. of sodium chloride, boiled for a few minutes, barely acidified with hydrochloric acid and filtered. The chloromercuri compound after drying-in the air weighed 140 g. It was stirred with 400 cc. of glacial acetic acid and treated at room temperature with a glacial acetic acid solution of 24 g. of chlorine. Reaction took place at once and most of the material went into solution. The mixture was heated to boiling and filtered from a slight residue. The filtrate on cooling and on concentration gave mixtures of acids which were separated by a careful series of fractional crystallizations using as solvents glacial acetic acid, water and xylene. The acid obtained in largest amount melted at 241–242°. This was 5-chloro-1-naphthoic acid. Its melting point was not lowered by mixing with some of the known acid.[3] Smaller amounts of 8-chloro-1-naphthoic acid[4] melting at 171–171.5° were obtained. A known sample of this acid was prepared by treating with chlorine anhydro-8-hydroxymercuri-1-naphthoic acid obtained from naphthalic acid.[5] It melted at 170–170.5°. A mixture of the two melted at 169–170". Examination of the optical properties of the two samples by means of the polarizing microscope also showed their identity. 8-Bromo-1-naphthoic acid, m, p. 176–179°, was made by a similar process.

The mother liquors from the 5-chloro and 8-chloro acids may have contained other acids but none could be isolated.

In a further search for other acids in the mixture it was decided to resort to a fractional distillation of the esters; consequently, 320 g. of the hydroxymercuri-1-naphthoic acids was treated with chlorine as above. The mixed acids were then refluxed with absolute methanol and dry hydrogen chloride for eleven hours. The oil left after the removal of the excess of methanol was washed with sodium carbonate solution. The acid obtained by acidifying the sodium carbonate solution was again treated with methanol and hydrogen chloride. Most of it failed to esterify; wt., 25 g. Several crystallizations from dilute acetic acid and from xylene gave crystals melting at 165–166°. A mixture with a slightly impure sample of known 8-chloro-1-naphthoic acid of m. p. 166–167° melted at 164.5–166.5°. A crystallographic examination proved the identity of the two materials. The interference colors were identical; both were biaxial. One axis of each had an index of refraction of 1.572 ± 0.003, while each had an index of refraction for the other axis between 1.635 and 1.740. To further prove the structure of this acid, a sample was chlorinated at room temperature in acetic acid using iodine as a catalyst. The product was 5,8-dichloro-1-naphthoic acid[6] melting at 186–187°.

The oily esters insoluble in sodium carbonate solution were dried by mixing with dry benzene and distilling off the benzene. The dry ester mixture was submitted to three

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[2] Hausemann, *Ber.*, 9,1520 (1876).

[3] Ekstrand, *ibid.*, **11**, 1604 (1878).

[4] Ekstrand, *J. prakt. Chem.*, [2]**38**, 148 (1889).

[5] Leuck, Perkins and Whitmore, THIS JOURNAL, 51, 1831 (1929).

[6] Ekstrand, *J. prakt. Chem.*, [2] **38**, 151, 255 (1889).

careful fractionations at 6-mm. pressure and a fourth at 4-mm. pressure. In this way four fractions were obtained.

FRACTION I. 6.2 g., b. p. 120–125° (4 mm.).—Hydrolysis gave mainly 1-naphthoic acid, m. p. 160–161°. A careful series of fractional crystallizations from boiling water failed to give any other acid. A mixture with known 1-naphthoic acid of m. p. 159° melted at 159–160°. The identity of the known 1-naphthoic acid and the acid from the ester fraction was further determined by crystallographic studies. Both crystallized from xylene in needles. Each had an extinction axis parallel to the long axis of the crystal. Each gave the same type of interference colors. Each had an index of refraction for one axis of 1.550 and for the other axis one above 1.740. A mixture of the acid with a sample of 8-chloro-1-naphthoic acid of m. p. 166–167° melted completely below 150°.

FRACTION II. 5.3 g., b. p. 125–130° (4 mm.).—This proved to be mainly impure 1-naphthoic acid. No other acid was isolated.

FRACTION III. 10.8 g., b. p. 131–133° (4 mm.).—On hydrolysis this gave mainly 5-chloro-1-naphthoic acid, m. p. 236–240°.

FRACTION IV. 10.8 g., b. p. 140–143° (4 mm.).—This gave 5-chloro-1-naphthoic acid, m. p. 244–245°. A mixture with known pure 5-chloro-1-naphthoic acid of m. p. 245–246° melted at 244–246°.

The alkali-insoluble product from the mercuration of 1-naphthoic acid was next studied. It reacted violently with an almost equal weight of bromine. From the tarry product there was obtained only a very small amount of a bromine compound, m. p. 124–146°. This may be impure 1,5-dibromonaphthalene. No other product could be separated from the tar.

Summary

1. Two satisfactory methods have been developed for making 1-naphthoic acid in quantity.
2. 1-Naphthoic acid is readily mercurated in the 5- and &positions, chiefly in the former.
3. During the mercuration some of the product loses carbon dioxide with the formation of an alkali-insoluble di-mercurated product of unknown structure.
4. 5-Bromo-1-naphthoic acid, 5-chloro-1-naphthoic acid and 8-chloro-1-naphthoic acid have been prepared from the mercury compounds.
5. 8-Chloro-1-naphthoic acid cannot be esterified even by long treatment with absolute methanol and dry hydrogen chloride.
6. A useful method has been developed for making 8-halogen-1-naphthalic acids from the mercuration product of naphthalic acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

THE HYDROLYSIS OF HYDROGEN CYANIDE BY ACIDS[1]

BY VERNON K. KRIEBLE AND JAMES G. MCNALLY

RECEIVED MARCH 20, 1929 PUBLISHED NOVEMBER 8, 1929

In 1909 Walker and Krieble[2] investigated the hydrolytic action of aqueous solutions of hydrochloric and sulfuric acids on amygdalin. Their experiments showed that when strong aqueous solutions of these acids were used their hydrolytic action was quite different. Hydrochloric acid attacked the nitrile group first while sulfuric acid showed little tendency to attack this group but readily removed the two glucose radicals with the formation of mandelonitrile. These experiments were the first ones, so far as we know, which showed radical differences between like concentrations of these acids in regard to their catalytic power on hydrolysis. The present investigation was undertaken to determine whether this is a characteristic peculiar to amygdalin or whether it is general for nitriles.

This communication takes up the hydrolysis of the simplest of all nitriles—hydrogen cyanide. The results with other nitriles will be treated in a future publication. Our results show that there is a marked difference in the rate at which hydrochloric, sulfuric and hydrobromic acids catalyze the hydrolysis of hydrogen cyanide and that the rate for hydrochloric acid increases very rapidly with an increase in concentration of this catalyst.

Preparation of Material and Method of Procedure

Preparation of Hydrogen Cyanide.—This substance was prepared by the usual methods of treating either sodium or potassium cyanide with moderately concentrated sulfuric acid and distilling off the nitrile. By adding a drop of dilute sulfuric acid to the distillate the hydrogen cyanide could be kept for several months without any appreciable change in appearance or concentration. The solution was standardized by either Liebig's soluble cyanide method or by the gravinietric method using the insoluble silver salt.

Procedure.—The hydrolysis was carried out in several different ways. The most satisfactory one was to mix cold standardized hydrogen cyanide with cold standardized acid in a beaker surrounded with salt and ice. From this beaker a series of pyrex test-tubes was filled. These tubes were then sealed off as near as possible to the liquid or else closed with a rubber stopper which was tied down to make a gas tight seal. It is obvious that it is necessary to have the tubes as nearly full as possible to reduce to a minimum the evaporation of the hydrogen cyanide into the air space. We found that our results were the same irrespective of the container used. The tubes were then placed in a constant temperature bath regulated to 0.1°. Tubes were taken out at various time intervals and analyzed for ammonium formate.

Method of Following the Hydrolysis.—The hydrolysis of hydrogen cyanide is usually expressed

$$HCN + H_2O = HCONH_2 \quad (1)$$

$$HCONH_2 + H_2O = HCOONH_4 \quad (2)$$

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[1] Read at the meeting of the American Chemical Society in Richmond, Virginia, April, 1927.

[2] Walker and Krieble, J. *Chem. Soc.*, **85**, **1369** (1909).

We were interested in the first reaction but we did not follow it directly. Experiments to be described later showed that the rate of the second reaction can be considered to be infinitely greater than the first, making it possible to follow the first by estimating the ammonium salt.[3] This was done by the well-known Folin aspiration method. Aliquot portions of the solution were pipetted into large pyrex test-tubes and an excess of sodium carbonate was added. Air freed of ammonia was sucked through this solution and then through standard acid. The excess acid was titrated and the amount of ammonium salt present calculated.

Experimental Results

Pigure 1 shows the action of 5 N hydrochloric and 5 N sulfuric acid containing 4% amygdalin at 25° in so far as the hydrolysis of the nitrile group in amygdalin is concerned. These results agree with those reported by Walker and Krieble, namely, that hydrochloric acid attacks the nitrile group much more readily than sulfuric acid.

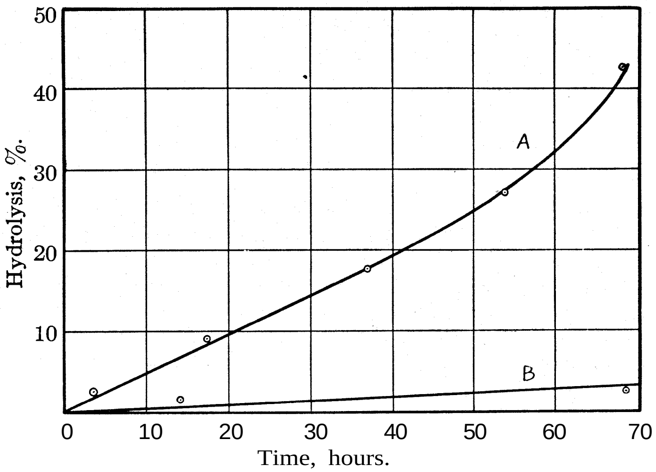

Fig. 1.—The hydrolysis of amygdalin at 25". A, 5 N HCI used as catalyst; B, 5 N H_2SO_4 used as catalyst.

In Pig. 2 we have the action of the same acids at the same concentration and temperature on hydrogen cyanide.[4] Here the difference in rates between these two acids is even more striking than with amygdalin. These two sets of experiments show that the nitrile hydrolysis does not follow the hydrogen-ion concentration of the solution in which the hydrolysis takes place. This conclusion is confirmed by examining a comparison of the rates of hydrolysis with different concentrations of hydrochloric acid. In Pig. **3** we have a comparison of 1.95 *N*, 3.92 *N*, 5.88 N and

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[3] Subsequent experiments by Mr. Blanchard showed that practically the same values are obtaineed when the disappearance of hydrogen cyanide is measured.

[4] The acid solutions in all of the experiments with hydrogen cyanide contained 0.7 moles of HCN per liter.

7.84 *N* hydrochloric acid solutions on hydrogen cyanide at 30°. The concentration of the acid has increased four-fold while the hydrogen-ion concentration has not increased that much but the time necessary to hydrolyze 25% of the hydrogen cyanide has increased a thousand-fold. We have studied the same reaction at 45°. The results are given in Fig. 4. The relative rates at this temperature for the various acid concentrations are similar to those at 30°. The temperature coefficient between 30 and 45° and between 45 and 65° is about 5. In Fig. 5 we have the comparison of 4 N hydrochloric acid and 4 *N* hydrobromic acid at 45°. Here we have two acids equally dissociated as measured by conductivity or by the lowering of the freezing point but the rate of hydrolysis where the hydrochloric

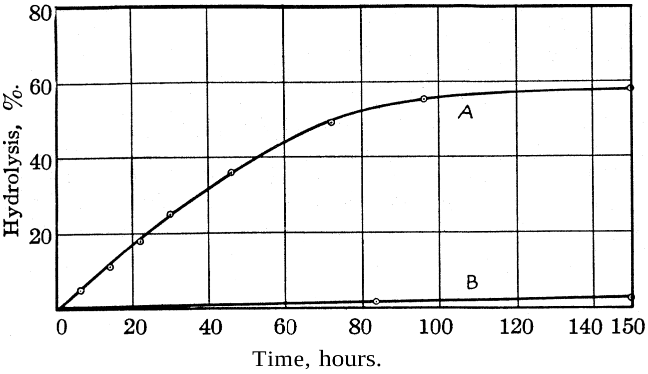

Fig. 2.—The hydrolysis of HCN at 25°. A, 5 N HCl used as catalyst; B, 5 N H_2SO_4 used as catalyst.

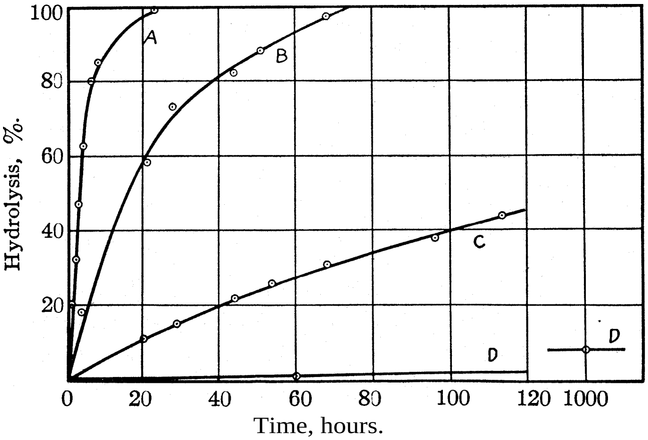

Fig. 3.—The hydrolysis of HCN at 30°. A, 7.84 N HCl used as catalyst; B, 5.88 N HCl; C, 3.92 N HCl; D, 1.95 N HCl.

acid is the catalyst is very much greater. This is in marked contrast with the hydrolysis of the corresponding amide. Figure 6 shows the rate of hydrolysis of formamide in the presence of 2 *N* hydrochloric acid and 2 *N* hydrobromic acid at 25°. In this case they are equally efficient as catalysts, as one would expect if the catalysis is due to the hydrogen ion. When the time required to hydrolyze 25% of hydrogen cyanide to formamide is compared with the time to hydrolyze 25% of formamide to ammonium formate in Figs. 3 and 6 the ratio is found to be 1400 hours to 6 minutes.

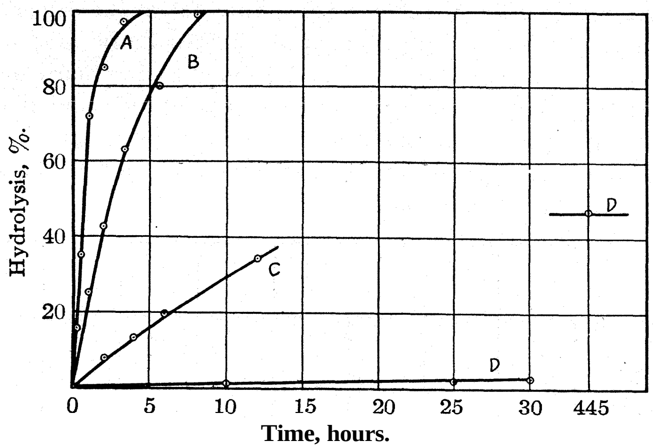

Fig. 4.—The hydrolysis of HCN at 45°. A, 7.84 N HCl used as catalyst; B, 5.88 N HCl; C, 3.92 N HCl; D, 1.95 N HCl.

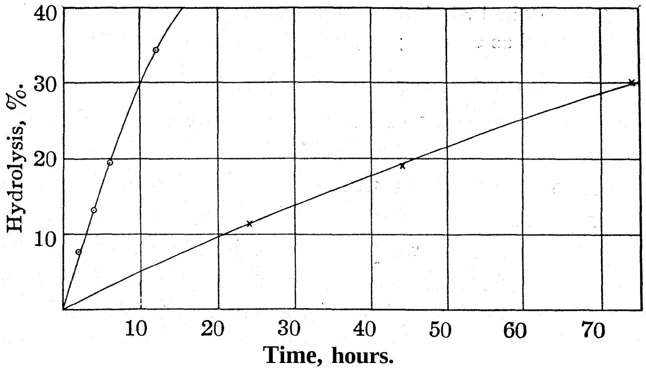

Fig. 5.—⊙, 4 N HCl at 45°; X, 4 N HBr at 45°.

The second molecule of water is therefore added on 14,000 times more rapidly than the first. These results on amide hydrolysis agree with those of other investigators, and when compared with the nitrile hydrolysis show conclusively that the mechanism for the two must be different.

Discussion of Results

No other hydrolytic reaction has been revealed in the literature where the rate went up so rapidly with increase in concentration. Blanksma[5] observed that in the transformation of acetylchloraminobenzene to p-chloro-acetanilide with hydrochloric acid as a catalyst the velocity changed as the square of the concentration of the hydrochloric acid.

Maass and Sivertz,[6] in studying the addition of hydrochloric acid to propylene, observed that the excess acid acted as a catalyst and that the rate increased very rapidly with small increases in concentration. These reactions are not hydrolytic reactions and, therefore, not of the same type described in this communication.

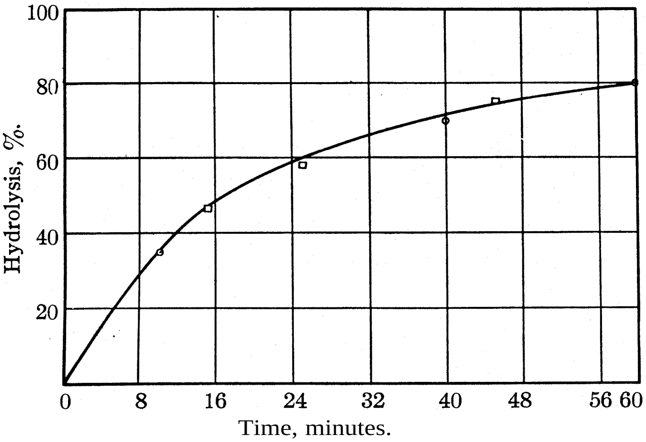

Fig. 6.—The hydrolysis of $HCONH_2$ at 25°. □, 2 M HCl used as catalyst; O, 2 M HBr used as catalyst.

A study of the change in rate with change in acid concentration in Fig. 3 shows that it is of the same order of magnitude as the change of activity of the undissociated hydrochloric acid molecule as indicated by electromotive-force measurements in the literature. To make more suitable the graphical representation of this relationship in Fig. 7 between velocity constants and the activities we plotted the logarithm of the velocity constants[7] for hydrochloric acid concentrations of 1.95, 3.92, 5.88 and 7.84 N as abscissa against the logarithm of the activities[8] for undissociated hydrochloric acid of the same concentrations. The velocity constants were calculated as described below from the data of experiments carried out

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[5] Blanksma, *Rec. trav. chim.*, 21,366 (1902); 22,290 (1902).

[6] Maass and Sivertz, THIS JOURNAL, 47,2883 (1925).

[7] Actually the logarithm of $K \times 10^5$ was plotted, which merely shifts the origin.

[8] The values for the activities used are those given by Lewis and Randall for 25°, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 336.

at 30, 45 and 65°. If the relationship were exact a straight line would be obtained.

This close relationship between the velocity of this reaction and the activity of the hydrogen chloride molecule calculated from physical measurements is remarkable. The literature does not record another like it so far as we know.[9] It suggests a combination between hydrogen cyanide and hydrogen chloride. That such a combination takes place in non-aqueous solutions is well known. A compound $2HCN\cdot 3HCl$ has been isolated in an ethyl acetate solution.[10] That an iminoformyl chloride $ClC{=}NH$ can also be formed is pretty well proved by Gattermann's reaction for the synthesis of aldehydes[11]

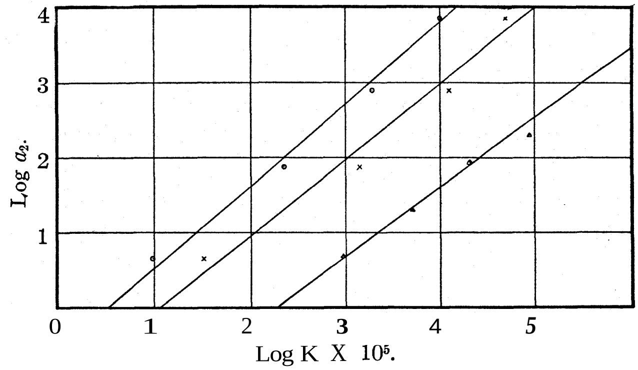
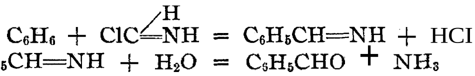
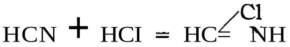


Fig. 7.—⊙, 30°; X, 45°; A, 65°.

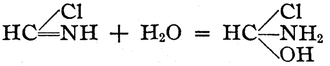


$$C_6H_6 + ClC\overset{H}{=}NH = C_6H_5CH{=}NH + HCl$$
$$C_6H_5CH{=}NH + H_2O = C_6H_5CHO + NH_3$$

Gautier[12] isolated a compound $HCN\cdot HCl$ by passing anhydrous hydrogen chloride into hydrogen cyanide at 35 to 40°. He found it to be a very unstable compound which decomposed spontaneously when added to water, producing formic acid. We, therefore, propose that the hydrolysis to the amide takes place through the following series of reactions



$$HCN + HCl = HC\overset{Cl}{=}NH \qquad (1)$$



$$HC\overset{Cl}{=}NH + H_2O = HC\begin{smallmatrix}Cl\\NH_2\\OH\end{smallmatrix} \qquad (2)$$

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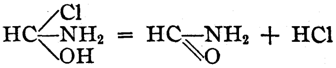
[9] Maass and Hiebert, This Journal, 46, 299 (1924), found that the decomposition of hydrogen peroxide was catalyzed by the undissociated hydrogen chloride molecule. Their velocity constant, however, did not vary with the activity of the hydrogen chloride molecule.

[10] N. S. Sidgwick, "The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1910, p. 199.

[11] Gattermann, *Ber.*, 31, 1149, 1765 (1898); *Ann.*, 347, 347 (1906); 357, 313 (1907).

[12] Gautier, *Ann. chim.* phys., [4] 17, 129 (1869).



$$\mathrm{HC(Cl)(NH_2)(OH)} = \mathrm{HC(=O)NH_2} + \mathrm{HCl} \tag{3}$$

Gautier found that his hydrogen chloride–hydrogen cyanide compound decomposed with almost explosive violence, so that Reactions 2 and 3 are very fast compared with 1. So the rate of hydrolysis is controlled by the rate of addition of hydrogen chloride to hydrogen cyanide, which in turn is a function of the number of hydrogen chloride molecules present in such a state that they can enter into the reaction. As the hydrogen chloride is only momentarily combined, its concentration for any given set of conditions is a constant; and as the amount of water present is very large, the reaction can for practical purposes be considered a monomolecular reaction. In Table I we have recorded the velocity constants for a few of our experiments calculated on the basis of a monomolecular reaction.

TABLE I

VELOCITY CONSTANTS

3.92 *N* HCl at 30°			7.84 *N* HCl at 30°		
Time, hours	% Hydrolyzed	K	Time, hours	% Hydrolyzed	K
4.08	1.9	0.0020	1	20.85	0.1015
21.13	10.75	.0023	1.91	32.92	.1010
28.33	14.87	.0024	2.71	46.96	.1011
48.33	21.7	.0024	4.26	69.50	.1220
53.75	25.6	.0024	5.65	78.33	.1175
68.12	31.15	.0024	6.88	82.99	.1118

We believe that the mechanism with hydrobromic acid as a catalyst is similar to that with hydrochloric acid. It is interesting to note that in non-hydrolytic reactions, hydrobromic acid has frequently been found to be more reactive than hydrochloric acid. Maass and Sivertz[13] found that hydrobromic acid added on to propylene 200 times faster than hydrochloric acid did. Acree and Johnson,[14] in studying the transformation of acetylchloro-aminobenzene to p-chloro-acetanilide, found that hydrobromic acid was 1000 times more effective than hydrochloric acid.

Whether sulfuric acid reacts in the same way as the halogen acids we shall be better able to say after we have studied it more thoroughly.[15]

Summary

The rates of hydrolysis of amygdalin and hydrogen cyanide when catalyzed by hydrochloric and sulfuric acids have been quantitatively studied. It is found that for 5 N concentrations hydrochloric acid hydrolyzes amygdalin ten times faster than sulfuric. For hydrogen cyanide the difference is even greater.

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[13] Ref. 6, p. 2888.

[14] Acree and Johnson, Am. Chem. J., 38, 274 (1907).

[15] Recent experiments by Mr. Peiker seem to show that the rate of hydrolysis passes through a minimum when the concentration of sulfuric acid is increased.

When the concentration of hydrochloric acid was varied from 1.95 N to 7.84 N, the velocity in the hydrogen cyanide hydrolysis increased about 1000 times. It is pointed out that this increase in velocity corresponds to the increase in activity for corresponding concentrations of the undissociated hydrogen chloride molecule as measured by electromotive force methods, and it is suggested that this increase in velocity is due to an increase in the concentration of activated hydrogen chloride molecules.

A 4 N hydrochloric acid solution is more than 6 times as effective in hydrolyzing hydrogen cyanide as a corresponding hydrobromic acid solution.

A tentative mechanism for the hydrolysis of hydrogen cyanide is proposed.

HARTFORD, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF WEST VIRGINIA UNIVERSITY AND THE JOHNS HOPKINS UNIVERSITY]

A METHOD OF COUPLING ORGANIC RADICALS BY MEAMS OF THE GRIGNARD REAGENT[1]

BY JOHN H. GARDNER AND P. BORGSTROM

RECEIVED APRIL 10, 1929 PUBLISHED NOVEMBER 8, 1929

The coupling of organic radicals by the action of heavy metal salts on organomagnesium compounds has been studied by a number of investigators.[2] However, the use of silver halides for this purpose has not been investigated, although Gilman and Kirby studied the action of certain Grignard reagents on silver cyanide. They observed the coupling of the organic radicals, the cyanide radical reacting as a halogen.[3]

We have investigated the application of the reaction of Grignard reagents with silver bromide to the preparation of symmetrical biaryls and bialkyls. A few preliminary experiments with cuprous chloride failed to give promising results. The bromide was selected in place of the chloride, as dry silver bromide is so little sensitive to light that it may be used in a fairly well lighted room.

The advantage of silver bromide over other heavy metal salts lies in the fact that it is easily prepared pure and dry. Its cost is compensated for by the fact that it can be recovered readily and almost completely. We have found the laboratory accumulation of silver residues *a* cheap and satisfactory source of silver bromide.[4]

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[1] The major part of this work was done while one of us (G.) was a National Research Fellow in Chemistry.

[2] Gilman and Parker, THIS JOURNAL, 46,2823 (1924), give a very complete review of the literature; see also Moyer and Adams, *ibid.*, 51, 630 (1929).

[3] Gilman and Kirby, *Rec. trav. chim.*, 48, 155 (1929).

[4] We are indebted to Mr. C. F. Brown of West Virginia University for the working up of silver residues into the bromide used in the early part of this work.

The procedure for the preparation of biaryls consists in adding the arylmagnesium halide to a well-stirred suspension of silver bromide in dry ether, adding benzene and decomposing the silver aryl first formed by heating to boiling for a short time. In the case of the alkylmagnesium halides, the silver alkyl which is probably first formed decomposes immediately with the formation of silver and bialkyl.

It has been found possible to prepare biphenyl and 4,4′-dimethoxybiphenyl in quite satisfactory yield by this method. Bi-*p*-tolyl was obtained in good yield and purity in a small run (0.05 mole), but on increasing the amount of the bromide to 0.35 mole the yield was reduced to 25%. Among the aliphatic and alicyclic compounds, *n*-octane, bibenzyl and bicyclohexyl were obtained in fair yield and satisfactory purity. In reacting silver bromide with the Grignard reagents prepared from *iso*- and *sec*-butyl bromides, no pure compounds could be isolated, the products distilling over a considerable range with no detectable break in the distillation curves. Whether this was due to side reactions during the formation of the Grignard reagents or during the reaction with silver bromide cannot at present be stated. This will be further investigated.

We believe that this procedure can be used to couple aryl and alkyl radicals whenever the Grignard reagents can be prepared without excessive side reactions. Obviously, if by-products resulting from intramolecular rearrangements during the formation of the Grignard reagent or the reaction with silver bromide are produced in too great amounts, it will be impossible to obtain a uniform product by this method.[5] It does, however, permit the preparation of symmetrical biaryls and certain bialkyls without the complicated side reactions encountered in the use of the Wurtz–Fittig reaction.[6]

Experimental

General Procedure.—The appropriate Grignard reagent was added, with stirring, to a suspension of the equivalent quantity of dry silver bromide in dry ether. The mixture was stirred for a half hour and then boiled under a reflux for an hour. In the case of the Grignard reagents derived from *p*-bromotoluene and *p*-bromo-anisole, a volume of benzene equal to that of the ether was added to raise the boiling point before refluxing. If the product was solid, the ether and the benzene if present were distilled off and the residue was treated with very dilute hydrochloric acid. After cooling, the mixture was filtered and the residue air dried. The product was extracted from the residue with hot alcohol and purified by distillation or by recrystallization from alcohol.

When the product was a liquid, dilute hydrochloric acid was added to the mixture after refluxing, the solvent and product were distilled off, dried over calcium chloride and distilled. The results are given in Table I.

The absence of the formation of any definite product from *iso*- and *sec*-butyl bromides may be due to intramolecular rearrangement on the

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[5] Compare Gilman and Fothergill, THIS JOURNAL, 50, 3334 (1928); Gilman and Kirby, *ibid.*, 51, 1571 (1929).

[6] Compare Bachmann and Clarke, ibid., 49, 2089 (1927).

TABLE I

RESULTS OF EXPERIMENTS

Halide	Amount, mole	Product	Yield G.	%	M. p. or b. p., °C.
Bromobenzene	1.0	Biphenyl	51	66	68.5 (m.) 250–254 (b.)
p-Bromotoluene	0.05	Bi-p-tolyl	3.3	72	117–119 (m.)
	.35		8	25	117–119 (m.)
p-Bromo-anisole	.35	Bi-*p*-anisyl	17.5	48	171-172 (m.)
Benzyl chloride	1.0	Bibenzyl	65	71	51 (m) 278 (b.)
Cyclohexyl bromide	1.0	Bi-cyclohexyl	25	40	232–234 (b.)
n-Butyl bromide	1.0	n-Octane	24	42	121–123 (b.)
Isobutyl bromide	1.0	......	..	..	89.5–110.5 (b.)
Sec.-butyl bromide	1.0				89–120.5 (b.)

part of free radicals formed by the interaction of the Grignard reagents with silver bromide, assuming the reaction to take place according to the equations

$$\mathrm{RMgX} + \mathrm{AgBr} = \mathrm{R} + \mathrm{Ag} + \mathrm{MgXBr}$$
$$2\mathrm{R} = \mathrm{R{-}R}$$

This is to be further investigated.

Preparation of Silver Bromide.—The silver bromide was precipitated from a warm solution of silver nitrate with sodium bromide, washed with water and with acetone and dried in an oven at a temperature not exceeding 80°. It is important that it be dried at a low temperature as a higher temperature, even 90°, results in larger particles and a less effective product.

Recovery of Silver Bromide.—The silver residues were reduced in the usual way with zinc and sulfuric acid to metallic silver which was converted into silver nitrate.

Summary

Biphenyl, bi-p-tolyl, bi-p-anisyl, bibenzyl, bi-cyclohexyl and *n*-octane have been prepared by the action of the appropriate Grignard reagent on silver bromide.

ST. LOUIS, MISSOURI
WASHINGTON, D. C.

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF MICHIGAN]

THE REDUCING ACTION OF ALIPHATIC GRIGNARD REAGENTS

BY F. F. BLICKE AND L. D. POWERS[1]

RECEIVED APRIL 20, 1929 PUBLISHED NOVEMBER 8, 1929

During the course of an investigation, we wished to prepare a number of tertiary carbinols from the interaction of alkylmagnesium halides and benzophenone. Methyl- and ethyldiphenylcarbinol can be obtained in good yields from methylmagnesium iodide and ethylmagnesium bromide, respectively, and benzophenone. Klages and Heilmann[2] state that n-propylmagnesium bromide reacts with the above ketone to form a compound which melts at 65°; this material they considered to be *n*-propyldiphenylcarbinol. When the carbinol was treated with hydrogen chloride a substance was formed which was described as propyldiphenylchloromethane. By reduction of the carbinol, diphenylbutane was supposed to have been produced. We found that the propyldiphenylcarbinol of Klages and Heilmann was, in reality, benzhydrol and that their propyldiphenylchloromethane and diphenylbutane were actually diphenylchloromethane and diphenylmethane, respectively.

In order to prepare propyldiphenylcarbinol Masson,[3] as well as Skraup and Freundlich,[4] allowed phenylmagnesium bromide to react with ethyl butyrate. The former investigator obtained an oil which boiled at 185° under 15-mm. pressure; the latter isolated a product, after distillation under greatly diminished pressure, which melted at 36°. Inasmuch as tertiary carbinols of the type under discussion lose water very readily, with the formation of an ethylene derivative, especially when subjected to heat, we decided to investigate further the compound obtained by Skraup and Freundlich. After the interaction of phenylmagnesium bromide and ethyl butyrate, at a low temperature, we were able to isolate, without distillation, a crystalline compound which melted at 33–35°. The carbinol nature of this substance was shown by the fact that it reacted with ethylmagnesium bromide with the evolution of ethane. Finally, we found that the compound obtained by the action of phenylmagnesium bromide on phenylpropyl ketone, undoubtedly propyldiphenylcarbinol, melted at 33–34°.

It seems remarkable that no secondary carbinol should be formed from the interaction of methylmagnesium iodide and benzophenone, very little from ethylmagnesium bromide and the ketone, while in the case of n-propylmagnesium bromide at least 50% of the benzophenone is converted

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[1] Parke, Davis and Company Fellow, 1926–1927.

[2] Klages and Heilmann, *Ber.*, 37, 1451 (1904).

[3] Masson, *Compt. rend.*, 135, 533 (1902).

[4] Skraup and Freundlich, *Ber.*, 55, 1078 (1922).

into benzhydrol, even though the reaction is carried out at 0°, as a result of the reducing action of the Grignard reagent.

A number of isolated instances of the reducing action of Grignard compounds have been reported from time to time.[5] However, since a systematic study to determine the relative reducing power of an homologous series of alkylmagnesium halides, especially with respect to a given ketone,[6] has not been made, we began an investigation of the action of various alkylmagnesium halides on benzophenone. This ketone is especially adapted for the purpose in view since it cannot enolize and the reduction product, benzhydrol, is a crystalline substance which can be purified and identified without difficulty. Our results are described in the experimental part of this paper.

It seems to us that the reducing action of aliphatic Grignard reagents toward various compounds can be accounted for if the assumption is made that trivalent carbon radicals are produced as intermediate reaction products.[7] It would be expected that these trivalent carbon radicals would be very unstable and that they might undergo, spontaneously, one of the types of transformation which have been found to be characteristic for trivalent carbon radicals of the triarylmethyl type, namely, addition, mutual oxidation and reduction, and polymerization.[8]

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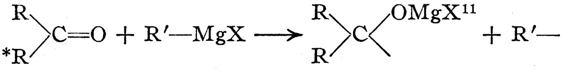
[5] The first observation of this type is that of Grignard (Doctor's "Dissertation," Annales de L'Université de Lyon, 1901, p. 48), who obtained not only phenyl*iso*amylcarbinol but also benzyl alcohol from iso-amylmagnesium bromide and benzaldehyde. Sabatier and Mailhe, *Compt.* rend., 139, **343** (1904); ***Bull.*** *soc.* chim., *[3]* 33, 79 (1905); Ann. chim. *phys.*, [8] 10, 540 (1907), noted that benzophenone and cyclohexylmagnesium chloride yielded benzhydrol and cyclohexene.

[6] Stas, ***Bull.*** *soc.* chim. ***Belg.***, 34, 188 (1925); ibid., 35, 379 (1926), has studied the action of a number of Grignard reagents on several aliphatic ketones; however, since aliphatic ketones may react in the enolic form with alkylmagnesium halides, these ketones are not entirely suitable for a study of the reducing action of Grignard compounds. Recent contributions to somewhat different phases of this subject have been made by the following investigators: Meisenheimer and Casper, Ber., 54, 1655 (1921); Hess and Rheinboldt, ibid., 54, 2043 (1921); Hess and Wustrow, Ann., 437, 256 (1924); Meisenheimer, ibid., 442, 180 (1925); Rheinboldt and Roleff, J. *prakt.* Chem., 109, 175 (1925); Conant and Blatt, THIS JOURNAL, 51, 1227 (1929).

[7] Späth, Monatsh., 34, 1967 (1913), and also Schlubach and Goes, ***Ber.***, 55, 2897 (1922), have already proposed such an explanation to account for the products which are formed when an alkyl- or arylmagnesium halide reacts with an organie halogen compound. Bachmann and Clarke, THIS JOURNAL, 49, 2089 (1927), have assumed the formation of radicals in the Wurtz-Fittig reaction and Wieland and co-workers, *Ber.*, 48, 1098 (1915); ibid., 55, 1816 (1922); Ann., 446, 31, 49 (1925); *ibid.*, 452, 1 (1926), have made an extensive study in order to determine, in certain instances, whether or not radicals are intermediate reaction products. Quite recently Gilman and Fothergill, THIS JOURNAL, 50, **3334** (1928), and Gilman and Kirby, ibid., 51, 1571 (1929), have made several observations on the mutual oxidation and reduction (disproportionation) of radicals.

[8] In some instances it has been found that triarylmethyls also undergo internal rearrangement.

In conformity with this hypothesis the interaction of a ketone and a Grignard reagent would be formulated as follows[9,10]



$$\begin{matrix}R \\ {}^{*}R\end{matrix}\!\!>\!C{=}O + R'{-}MgX \longrightarrow \begin{matrix}R \\ R\end{matrix}\!\!>\!C\!<\!\begin{matrix}OMgX^{11} \\ \end{matrix} + R'{-}$$

I II

The radicals I[12] and II may unite (addition) to form the addition product $R_2C(OMgX)R'$ which, upon the addition of water, would yield a tertiary carbinol; they may undergo mutual oxidation and reduction with the production of $R_2C(OMgX)H$, the magnesium halide derivative of a secondary carbinol, and the unsaturated hydrocarbon R'_{-H}; or, finally, they may polymerize to dimolecular forms $R_2C(OMgX){-}R_2C(OMgX)$ and $R'{-}R'$; the former when treated with water would yield a pinacol,[13] the latter product represents a saturated hydrocarbon.[14]

Experimental Part

Propyldiphenylcarbinol.—Ethyl butyrate, dissolved in benzene, was added to approximately three molecular equivalents of phenylmagnesium bromide which had been cooled to 0°. After twenty-four hours the reaction mixture was decomposed with ice and ammonium chloride. The oily product which was obtained became crystalline after it had been cooled to a low temperature for some time. The material was so soluble that it could not be recrystallized but after it had been washed with petroleum ether (20–40°) it melted at 33–34°.

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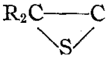
[9] This mechanism applies also to the reaction between a Grignard compound and an aldehyde or an ester. If an aldehyde is used R* is to be replaced by H, in the case of an ester by OR.

[10] It is possible that a molecular addition product may be formed first in all instances.

[11] Radicals of this type have been formulated by Lagrave, *Ann. chim.*, [10] *8*, **372 (1927).**

[12] Compounds of Type I seem to be formed by the action of iodine and magnesium on ketones [Gomberg and Bachmann, THIS JOURNAL, **49, 238 (1927);** *ibid.*, **50, 2762** (1928)] and sodium analogs have been described by Schlenk and co-workers *[Ber.*, **44, 1182 (1911);** *ibid.*, **46, 2840 (1913);** *ibid.*, **47, 486 (1914);** *Ann.*, **463, 1** (1928)]; and by Blicke [THIS JOURNAL, **46,2560 (1924);** *ibid.*, **47,229** (1925)].

[13] An example of what appears to be pinacol formation in the Grignard synthesis has been recorded by Barnett, Cook and Nixon [*J. Chem. Soc.*, *131,* **505** (1927)]. It has been shown by Schonberg and co-workers *[Ber.*, **58, 1796 (1925);** *ibid.*, **60, 235 (1927);** *Ann.*, **454, 37** (1927)] that thioketones react with Grignard reagents to form sulfides of the type  $\underset{\diagdown S \diagup}{R_2C{-\!-\!-}CR_2}$. These sulfides, analogs of α-pinacolines, are formed, undoubtedly, through loss of $XMg{-}S{-}MgX$ from the compound $R_2C(SMgX){-}C(SMgX)R_2$, the dimolecular form of the initial reaction product $R_2C(SMgX){-}$.

[14] The radical $R'{-}$ instead of polymerizing might also undergo oxidation and reduction with the formation of equivalent amounts of the saturated hydrocarbon R'_{+H} and the unsaturated hydrocarbon R'_{-H}.

Phenylpropyl ketone,[15] dissolved in benzene, was added in small portions to a cold ether solution of phenylmagnesium bromide which had been prepared from 1.2 molecular equivalents of bromobenzene. After twenty-four hours the liquid was decanted from the precipitate and the latter was treated with ice and ammonium chloride. After the oily reaction product had been cooled for several days it became solid. The material was washed with low-boiling petroleum ether; m. p. 32–33°.

Reducing Action of Alkylmagnesium Halides.—It is not a simple matter to determine quantitatively the relative reducing power of a series of alkylmagnesium halides. The yields of the latter compounds vary greatly, depending upon the nature of the alkyl halide and other factors, and a complete separation of the secondary carbinol from the tertiary carbinol and other products present in the reaction mixture is a difficult process. In order to isolate benzhydrol we made use of the fact that the MgBr derivative of this carbinol is quite insoluble in a mixture of benzene and ether. To ethylmagnesium bromide, prepared from 13.1 g. of ethyl bromide, 2.9 g. of magnesium and 25 cc. of ether, there was added 9.2 g. of benzhydrol dissolved in 25 cc. of benzene. After twelve hours the precipitate was separated from the ether–benzene layer and decomposed with ice and ammonium chloride. There was obtained 7.5 g. of benzhydrol or 81% of that used originally, which melted at 64–66° without recrystallization.

Procedure.—The ketone, dissolved in the smallest possible amount of dry benzene, was added in small portions with vigorous agitation to an ether solution of the Grignard reagent which had been thoroughly cooled with ice. After twenty-four hours the reaction mixture was treated with ice and ammonium chloride. In those instances in which a precipitate had formed the latter was isolated and decomposed separately. The ether–benzene solution was dried with fused sodium sulfate and the solvents were then allowed to evaporate spontaneously.

In addition to the crystalline secondary carbinols there were obtained in most cases oils from which some solid material deposited after a number of days.

Undoubtedly the reduction of the ketones took place to a greater extent than is indicated in the above table. Some of the secondary carbinol was lost during the final purification and a certain amount could not be separated from other products formed in the reaction. The five-degree range in the melting point of the benzhydrol, obtained from benzophenone and *iso*butylmagnesium iodide, shows that the material was impure; hence the yield recorded is somewhat too high. In all other instances it can be seen from the melting points that the yields of the secondary carbinols are based on quite pure material.

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[15] Sorge, *Ber.*, **35**, 1073 (1902).

TABLE I

RESULTS OF EXPERIMENTS

Alkylmagnesium halide prepared from		Yield of secondary carbinol based on ketone, %	M. p., °C. Found	M. p., °C. Literature	Mixed m. p., °C.
Methyl iodide	Benzophenone	97[a]	...	...	...
Ethyl bromide	Benzophenone	80[b]	...	...	...
n-Propyl bromide	Benzophenone	50[c]	67–68	68[d]	67–68
Isopropyl bromide	Benzophenone	22	65-66	...	...
n-Butyl iodide	Benzophenone	27	65-67	...	...
Isobutyl iodide	Benzophenone	74	61–66	...	...
Iso-amyl bromide	Benzophenone	30	63-67	...	...
n-Propyl bromide	*p*-Bromobenzophenone[e]	24	62–64	63[f]	63–64
n-Propyl bromide	Phenyl-α-naphthyl[g]	65	84–86	86[h]	84–86
n-Propyl bromide	Phenylbiphenyl[i]	48	94–96	96[j]	95–96
n-Propyl bromide	Phenylbenzyl[k]	9	64-66	66-67'	64–65

[a] Tertiary carbinol. There was used **0.025** mole of benzophenone and 0.100 mole of methyl iodide. The tertiary carbinol melted at **81–82'.** Klages [*Ber.*, **35**, **2646 (1902)**] recorded the melting point as **81°**. Schmalfuss [*J. prakt. chem.*, **108**, *88* **(1924)**] reported a 98% yield of this carbinol.

[b] Tertiary carbinol. **0.025** mole of benzophenone and **0.100** mole of ethyl bromide. The tertiary carbinol was recrystallized from a mixture of benzene and low-boiling petroleum ether; m. p. **92–94".** Masson [*Compt. rend.*, **135**, **533** (1902)] prepared ethyldiphenylcarbinol from phenylmagnesium bromide and ethyl propionate; m. p. 91°. Hell and Bauer [*Ber.*, **37**, **231** (1904)] obtained the compound from ethylmagnesium bromide and benzophenone but did not report the yield; m. p. **94–95'.**

[c] In this experiment, as well as in those which follow, there were used **0.100** mole of ketone and **0.120** mole of the alkyl halide.

[d] A sample of benzhydrol was prepared from phenylmagnesium bromide and ethyl formate Masson [Compt. *rend.*, **135**, **533** (1902)]. A part of the benzhydrol obtained as a reduction product was converted by hydrogen chloride into benzhydryl chloride. The latter was dissolved in benzene and shaken with silver benzoate. The benzhydryl benzoate formed melted at **86–88'.** Linnemann [*Ann.*, **133**, **20 (1865)** prepared this benzoate by another method; m. p. **87-89".**

[e] Montagne, Rec. *trav. chim.*, **27**, **335 (1908).**

[f] Montagne, *ibid.*, **27**, *342* **(1908).**

[g] Phenyl-a-naphthyl ketone was prepared by the addition of **20.6** g. of phenyl cyanide, drop by drop, to a-naphthylmagnesium bromide which had been prepared from **49.6** g. of a-bromonaphthalene and **5.8** g. of magnesium. The mixture was heated for one hour on a water-bath, the heavy precipitate removed by filtration and decomposed in the usual manner. The ketone imine was boiled for several hours with a mixture composed of water, acetic acid and sulfuric acid. The crude ketone which was formed was subjected to steam distillation in order to remove traces of naphthalene and phenyl cyanide and was then distilled under diminished pressure. The product melted at **71–73°**.

[h] A much better procedure for the preparation of phenyl-α-naphthylcarbinol than that described by Acree [*Ber.*, **37**, **2757** (1904)] is as follows: **10.6** g. of pure benzaldehyde, diluted with four volumes of absolute ether, was added slowly to the Grignard reagent obtained from **24.8** g. of a-bromonaphthalene and **2.9** g. of magnesium. After twenty-four hours the precipitate was filtered and decomposed with ice and ammonium chloride. The crude product was recrystallized from a mixture of benzene and petroleum ether. The yield of pure carbinol was **16** g.

[i] Montagne, *Rec. trav. chim.*, *27, 356* (1908).
[j] Montagne, ibid., 27, 358 (1908).
[k] Sudborough, J. *Chem. Soc.*, 71,219 (1897).
[l] Hell, *Ber.*, 37, 456 (1904).

In one instance 36.4 g. of benzophenone, dissolved in benzene, was allowed to react with 1.2 molecular equivalents of n-propylmagnesium bromide at approximately 0°. The gas evolved during the reaction was collected over mercury and then passed through bromine dissolved in carbon tetrachloride. Nine and four-tenths g. of propylene bromide was obtained which corresponds to a 23% yield. The bromide boiled from 135–140°. Undoubtedly a considerable part of the propylene remained dissolved in the reaction mixture.

An attempt was made to obtain the carbinol chloride from methyldiphenylcarbinol. The latter was dissolved in absolute ether and the solution was saturated with dry hydrogen chloride. After several days the solvent was removed at ordinary temperature by means of a stream of dry air. An oily residue was obtained, a part of which eventually became crystalline. The oil possessed a penetrating, camphoraceous odor. The crystalline material, after recrystallization from low-boiling petroleum ether, melted at 113–114°. This compound seems to be a polymerized form of 1,1-diphenylethylene and has been obtained by other investigators by a different method.[16]

Summary

It has been shown that a number of diarylalkylcarbinols cannot be made satisfactorily by the interaction of an alkylmagnesium halide and an aromatic ketone because of the reducing action of the Grignard reagent.

A mechanism has been suggested to account for the formation of the compounds produced in the above-mentioned reaction.

ANN ARBOR, MICHIGAN

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[16] Lebedew, Andreewsky and Matyuschkina, *Ber.*, 56, 2349 (1923); Kauffmann [*Z. physik.* Chem., 55, 557 (1905)] made a number of substituted ethylenes by the action of hydrogen chloride on tertiary carbinols.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF GEORGETOWN (KENTUCKY) COLLEGE]

THE EFFECT OF TEMPERATURE ON THE REDUCTION RATE OF FURFURAL WITH THE CATALYST FROM $PtO_2 \cdot H_2O$

BY J. STANTON PIERCE AND CHARLEY PARKS

RECEIVED APRIL 26, 1929 PUBLISHED NOVEMBER 8, 1929

Several investigators have noted a decrease in the catalytic activity of platinum black and sponge for hydrogenations when these are heated to a high temperature.[1] Others have noted that temperature affects reduction rates, both with[2] and without[3] the use of a solvent. However, little work has been done on a quantitative study of reduction rate, with platinum black, at temperatures slightly above and below room temperature, which is used generally in such reductions.

This paper deals with the effect of temperature on the reduction rate of furfural, in 95% alcohol, at 0, 20, 40 and 60°, with platinum black from $PtO_2 \cdot H_2O$[4] as catalyst. Using the same catalyst, Carothers and Jones[5] noted that between 50 and 100° increase in temperature caused increased speed in the reduction of aromatic nitriles. Tuley and Adams[6] observed that a rise in temperature caused an increase in the reduction rate of cinnamyl aldehyde, but a lowering of the yield of pure reduction product. Also, with this catalyst, it has been noted that the reduction rates of geraniol,[7] triphenylamine,[8] pyridine hydrochloride,[9] and aromatic nitro compounds[10] increase with rise in temperature, but these studies were not quantitative.

In this paper it is shown that increase in temperature from 0 to 40° causes a marked increase in the reduction rate of furfural, and at 60°, if sufficient catalyst is present, the initial reduction rate is much greater than at 40°. However, at 60° the catalyst is rendered inactive more readily than at 40°, so particularly if only a small amount of catalyst is present, the reduction will proceed faster at 40° than at 60°. Also, it

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[1] Vavon, *Compt. rend.*, 158, 409 (1914); Wright and Smith, *J. Chem. Soc.*, 119, 1683 (1921); Lemoine, *Compt. rend.*, 162,657 (1916).

[2] Paal and Gerum, *Ber.*, 40, 2209 (1907); Willstatter and Waldschmidt-Leitz, *ibid.*, **54B**, 113 (1921); Boeseken, van der Weide and Mom, *Rec. trav. chim.*, *35*, 260 (1915); Hiers and Adams, *Ber.*, **59B**, 162 (1926).

[3] Zelinsky and Turowa-Pollak, *Ber.*, **58B**, 1298 (1925); Escourrou, *Parfums de France, No.* 26, p. 86; Zelinsky and Borisoff, *Ber.*, **57B**, 150 (1924).

[4] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

[5] Carothers and Jones, *ibid.*, 47,3053 (1925).

[6] Tuley with Adams, *ibid.*, 47,3066 (1925).

[7] Adams and Garvey, *ibid.*, 48,480 (1926).

[8] Hiers and Adams, *ibid.*, 49, 1101 (1927).

[9] Hamilton and Adams, *ibid.*, 50,2261 (1928).

[10] Adams, Cohen and Rees, *ibid.*, 49, 1094 (1927).

is shown that, although furyl alcohol is formed readily and quantitatively, without activation of the catalyst, the same catalyst, without activation, will not add hydrogen to the formed furyl alcohol.

Experimental Part

The apparatus used in this work was essentially the same as that used by Vorhees and Adams,[11] except that it was arranged so that the temperature could be kept constant. In order that the results might be comparable, in each case 9.6 g. (0.1 mole) of furfural, dissolved in 75 cc. of alcohol, was reduced in the presence of catalyst from the same batch and 1 cc. of freshly prepared 0.1 M ferrous sulfate, with hydrogen at about 2 atmospheres pressure. Runs were made with 0.122 (see Fig. 1) and 0.244 g. (see Fig. 2) of $PtO_2 \cdot H_2O$[12] at 0, 20, 40 and 60°. In all of these reductions the catalyst was activated at the end of each hour by shaking it for ten minutes with oxygen.[13] The effect on the reduction rate may be noted from the upward trend of each curve at the beginning of the hour, in Figs. 1 and 2.

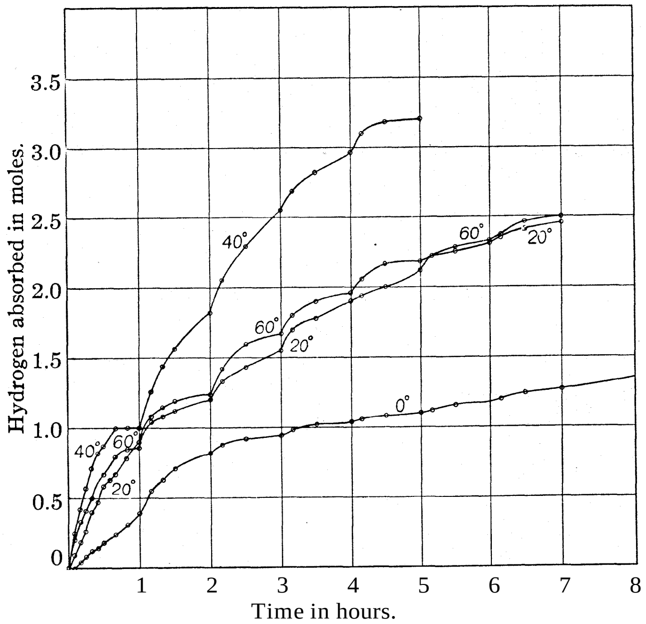

Fig. 1.—Reduction of 0.1 mole of furfural; 0.122 *g.* of catalyst; 1 cc. of *M*/10 ferrous sulfate.

Furyl alcohol was formed quantitatively by the addition of 1 mole of hydrogen to furfural. Kaufmann and Adams[13] showed that with the catalyst used for this work, on complete reduction, furfural yields tetrahydrofuryl alcohol, pentanediol-1,5, pentanediol-4,5 and n-amyl alcohol.

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[11] Vorhees with Adams, THIS JOURNAL, 44, 1403 (1922).

[12] Note: 0.122 g. of catalyst is 0.005 mole, assuming its formula to be $PtO_2 \cdot H_2O$. Calcd. for $PtO_2 \cdot H_2O$: Pt, 79.95. Found: Pt, 79.73.

[13] Kaufmann with Adams, THIS JOURNAL, 45, 3029 (1923).

As can be seen from the figures, the catalyst becomes active and the absorption of hydrogen becomes rapid much more quickly in the higher temperature than in the lower temperature reductions. $PtO_2 \cdot H_2O$ is brown and the active catalyst is black, so the change in color from brown to black is an indication of the formation of the active catalyst. Usually, in the 60° runs, the catalyst became black in less than forty-five seconds, while in the 0° runs it sometimes took ten minutes or over for the catalyst to become completely black.

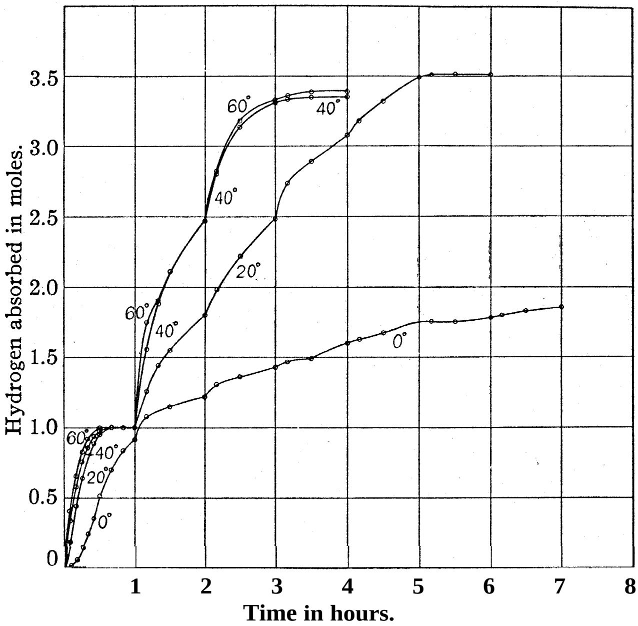

Fig. 2.—Reduction of 0.1 mole of furfural; 0.244 g. of catalyst; 1 cc. of $M/10$ ferrous sulfate.

It was noted that in no case was over 1 mole of hydrogen added to furfural until the catalyst was activated. Attempts were made to cause more to be absorbed by increasing the amount of catalyst and lengthening the time of shaking the reaction mixture. Although 0.122 g. of catalyst at 40° caused 1 mole of hydrogen to be added smoothly in forty minutes, at the same temperature 0.976 g. or eight times as much catalyst caused no more to be added (if a correction is made for the hydrogen required to reduce the $PtO_2 \cdot H_2O$ to the active catalyst, as determined in a control test), although the reaction mixture was shaken for one hour after hydrogen ceased to be absorbed. These facts seem to indicate that the platinum black which has been used as a catalyst for the reduction of furfural is not a catalyst for the reduction of furyl alcohol, and that the only way it can be made to add more hydrogen to the latter compound is to change its surface by activation.

Summary

1. Curves are given for the reduction rate of furfural at **0, 20, 40** and 60°.
2. Activation of the catalyst is necessary to add more than 1 mole of hydrogen to furfural.

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[CONTRIBUTION PROM THE CHEMICAL LABORATORY OP THE UNIVERSITY OP CALIFORNIA]

THE PREPARATION OF MERCURY DIPHENYL[1] BY USE OF THE GRIGNARD REAGENT

BY P. BORGSTROM AND MARGARET M. DEWAR

RECEIVED APRIL 26, 1929 PUBLISHED NOVEMBER 8, 1929

The reactions that may take place in the preparation of mercury diphenyl by the Grignard reagent are as follows

$$\begin{aligned}
HgX_2 + 2C_6H_5MgBr &= Hg(C_6H_5)_2 + 2MgBrX \qquad (1)\\
HgX_2 + C_6H_5MgBr &= Hg(C_6H_5)Hal + MgBrX\\
Hg(C_6H_5)X + C_6H_5MgBr &= Hg(C_6H_5)_2 + MgBrX\\
HgX_2 + Hg(C_6H_5)_2 &= 2Hg(C_6H_5)X
\end{aligned}$$

HgX_2 may be the iodide, bromide or chloride. Laszczynski[2] measured the solubility of mercuric iodide and chloride in absolute ether at 0° and found it to be **0.62** and 5.98%, respectively. Measurements made on mercuric bromide at 0° gave the solubility as 4.82 g. per **100** g. of solution, using absolute ether. Due to the insolubility of the iodide experiments were made with the bromide and chloride only. The yields as given in Table I show some difference between the bromide and chloride for the same concentration but not sufficient to say that one is much better than the other.

Table I shows that 85 mole per cent. of mercuric halide gives the best yield with the methods used. From published data[3] the yield of the Grignard reagent from bromobenzene is about 94%, which gives an excess over the mercuric halide used of about 9%; this is not too much considering the fact that it must be transferred before using.

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[1] For the different methods of preparation of mercury diphenyl see "Organic Syntheses," Vol. IX, John Wiley and Sons, Inc., New York, 1929, p. 54. One later method is described in *Ber.*, 62, 1018 (1929). The method in "Organic Syntheses" uses a 3% sodium amalgam. Better yields can be obtained with an 8% amalgam (Michaelis and Loesner, *Ber.*, 27, 264 (1894)) which has been checked by the authors. If a large quantity of mercury diphenyl is wanted this method is recommended over the Grignard. It should always be remembered that the vapors of mercury diphenyl are toxic.

[2] Laszczynski, *Ber.*, 27, 2285 (1894).

[3] Gilman, Zoellner and Dickey, THIS JOURNAL, 51, 1584 (1929).

Hilpert and Grüttner[4] give the yield for Equation 2. They refluxed for four hours 0.16 M phenylmagnesium bromide and 0.20 M mercuric bromide with a yield of recrystallized mercury phenyl bromide of 93%, or nearly quantitative. They state that this was easily prepared but to go from it to mercury diphenyl as shown in Equation *3* required an excess of the Grignard reagent and then gave a poor yield with 40% as the highest (no experiments cited).

From experimental evidence given in this paper the yield in Equation **3** is very close in agreement with the mercury diphenyl formation from mercury dihalide itself and may be the controlling factor in its preparation. The reverse reaction of Equation **3** is probably not sufficient to affect the yield in the presence of the excess Grignard reagent.

Equation 4 shows that if there is once any excess of mercury dihalide and mercury diphenyl present without the Grignard reagent there will be a loss of mercury diphenyl. This was substantiated by experiment.

Fleck[5] studied the reaction between mercury diphenyl and magnesium metal and found a reaction at about 200° with the formation of magnesium diphenyl and free mercury. It may be that this same reaction occurs to a less extent at the boiling point of ether, for if any unreacted magnesium is allowed to remain in the reaction flask the yield is greatly reduced.

Therefore the ideal condition for a large yield for the preparation of mercury diphenyl is as follows: have Grignard reagent in excess, have no magnesium metal present, do not let the mercury diphenyl formed stand with mercuric halide without the presence of the Grignard reagent and use about *85* mole per cent. of mercuric salts.[6]

TABLE I

YIELD OF MERCURY DIPHENYL WITH VARYING CONCENTRATIONS OF MERCURIC HALIDES

	Mercuric chloride			Mercuric bromide		
Runs	3	1	2	1	2	1
HgX_2, moles	0.375	0.425	0.45	0.188	0.415	0.225
C_6H_5Br, moles	1	1	1	0.5	1	0.5
$Hg(C_6H_5)_2$, moles	0.177	0.217	0.174	0.070	0.226	0.096
$Hg(C_6H_5)_2/HgX_2$ X 100	47.2	51.0	38.7	37.2	54.6	42.6

Experimental

Preparation of Mercury Diphenyl.—To the Grignard reagent, which was poured into a dry two-liter flask to separate it from the unreacted magnesium, was added the dried mercuric halide. After the slight reaction had subsided, it was refluxed for seventy-two hours. At the end of the reaction there was usually a gray residue in the flask

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[4] Hilpert and Gruttner, Ber., 46, 1675 (1913).

[5] Fleck, *Ann.*, 276, 138 (1893).

[6] These experiments were made without the use of mechanical stirrers, Soxhlet [see Gilman and Brown, THIS JOURNAL, 51,928 (1929)], etc., which are now used. The yield should be improved by their use.

with some unreacted mercuric halide. The ether layer was then poured while warm onto ice. White needles separated which were washed and dried. The contents of the flask were washed with 500 cc. of wet ether and the ether extract was washed with a very little dilute hydrochloric acid. The ether was evaporated and crystals of mercury diphenyl separated. The crude mercury diphenyl was dissolved in warm chloroform to which was added an equal volume of warm alcohol; it then was allowed to crystallize. The residue in the flask contained some mercury phenyl halide which could be extracted with hot xylene. The yields are given in Table I.

In one run using 0.75 mole quantity of mercuric chloride and 1.0 mole of bromobenzene, the Grignard reagent was not poured from the magnesium residues. The procedure was the same as with the others. The yield was reduced 15%.

In one run using 0.9 mole quantity mercuric chloride and 1 mole of the Grignard reagent, the experiment was conducted as usual except that the ether was cooled before pouring off from the residues. Crystals of mercury diphenyl separated. Then more ether was added and the contents of the flask was refluxed for several hours. On separation and evaporation of the ether no further mercury diphenyl was recovered and the yield was reduced over 5%. This decrease was probably due to the reaction between mercury diphenyl and the excess mercuric chloride to form mercury phenyl chloride.

Mercury Phenyl Chloride and **Phenylmagnesium** Bromide.—To 0.1 M Grignard (made and poured from the magnesium residues) was added 26.5 g. (0.085 mole) of recrystallized mercury phenyl chloride. There was a slight reaction on addition. This was gently refluxed for seventy-two hours as usual. The reaction product was handled as in the typical case; yield, 15.7 g. of recrystallized mercury diphenyl or 52.2% conversion based on the mercury phenyl chloride used.

Mercury Diphenyl and Mercuric Bromide.—Eighteen grams of recrystallized mercuric bromide and 17.7 g. of mercury diphenyl were gently refluxed in 250 cc. of dry ether for seventy-two hours. The ether was poured off and evaporated. A few tenths of a gram of mercury diphenyl was recovered. There is practically complete conversion to mercury phenyl bromide.

Mercury Diphenyl and Anhydrous Magnesium Bromide.—One hundredth mole of mercury diphenyl in 50 cc. of dry ether was refluxed with anhydrous magnesium bromide for several days. Then dried Michler's ketone was added and it was again refluxed. No color developed with the ketone on decomposition with water, showing no appreciable amount of the Grignard reagent present.'

Summary

The preparation of mercury diphenyl by the Grignard reagent and mercuric halides has been discussed. Some factors influencing the yield are given.

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Gilman and Schulze, THIS JOURNAL, 47,2002 (1925), give the test with Michler's ketone as a qualitative one for the Grignard reagent, but point out that the Grignard reagent might be present in small quantities and still be negative. The results here were either negative or at best a trace. As the magnesium bromide used was prepared by heating $MgBr_2 \cdot 6H_2O$ and NH_4Br in an atmosphere of dry carbon dioxide, it may not have been absolutely pure. This reaction is being studied further.

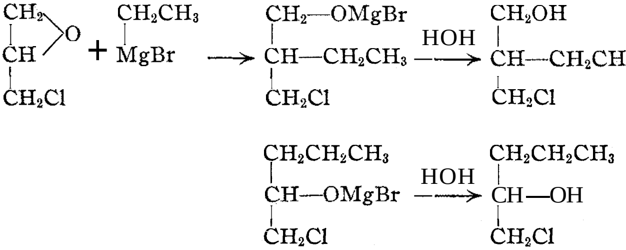
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE REACTION OF ETHYLMAGNESIUM BROMIDE WITH EPICHLOROHYDRIN

BY C. FREDERICK KOELSCH AND S. M. McELVAIN

RECEIVED MAY 2, 1929 PUBLISHED NOVEMBER 8, 1929

In connection with some work being carried on in this Laboratory it was desired to prepare 2-chloromethylbutanol-1 (I). It was thought that the reaction between ethylmagnesium bromide and epichlorohydrin might yield this particular compound, its isomer (11),or both, according to the reactions



(I)

(II)

The reaction was carried out in the usual manner, but when the reaction product was isolated and weighed it was apparent that the reaction had taken a different course from that shown above, for if the product formed was considered to be a chloro-amyl alcohol, the yield was approximately 115% of the theoretical.

The literature was then consulted, and it was found that the above reaction had been studied by a number of investigators, and that there was considerable disagreement as to the products that were formed. Iozitsch[1] reported that he obtained a chloro-amyl alcohol from the reaction between ethylmagnesium bromide and epichlorohydrin but made no mention of any other products. A little later Kling,[2] using methylmagnesium iodide to react with epichlorohydrin, obtained nothing but a glycerol chloro-iodohydrin. Iozitsch repeated his work and stated that he did obtain a glycerol chlorobromohydrin, but that he was able to separate it from the chloro-amyl alcohol by fractional distillation. The yield of neither product was given. Later, Fourneau and Tiffeneau[3] studied the action of ethyl-, propyl-, butyl- and amylmagnesium bromides on

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[1] The papers of Iozitsch on this subject are J. *Russ. Phys.-Chem. Soc.*, 34, 96 (1902); *ibid.*, 36, 6 (1904); but this journal was not available for reference. Neither could reference to this author's work be found in the *Centralblatt* or in the *British Chemical Abstracts*. *All* of the information concerning Iozitsch's work was found in the articles of Kling and of Fourneau and Tiffeneau.

[2] Kling, *Bull. soc. chim.*, [3] *31*, 14 (1904).

[3] Fourneau and Tiffeneau, *ibid.*, [4] 1, 1227 (1907).

epichlorohydrin under numerous conditions of reaction, and were unable to duplicate Iozitsch's results. Glycerol chlorobromohydrin was the only product that they could isolate from the reaction mixture regardless of which alkylmagnesium bromide was used. These investigators were able, however, to obtain good yields of the expected chloro-alcohols when phenyl-, p-methoxyphenyl- and benzylmagnesium bromides were used instead of the alkylmagnesium bromides, although there was always some glycerol chlorobromohydrin formed. Delaby[4] reported that ethylmagnesium bromide and ethyl glycerol epibromohydrin reacted to form 1,3-dibromopentanol-2, which corresponds to the results obtained by Fourneau and Tiffeneau, and by Kling.

An investigation of the reaction product from ethylmagnesium bromide and epichlorohydrin in this Laboratory showed the presence of at least two different compounds. On repeated fractional distillation under reduced pressure, the product was separated into two fractions, one boiling at 70–75° (20 mm.) and the other boiling at 100–105° (20 mm.). Analyses of these two fractions indicated that the lower-boiling fraction was a chloro-amyl alcohol, and that the higher-boiling fraction was a glycerol chlorobromohydrin. This latter compound was proved to be 1-chloro-3-bromopropanol-2 by preparing the known 1,3-diphenoxypropanol-2 from it.

Since Iozitsch did not determine the structure of the chloro-amyl alcohol which he prepared, the product obtained in this work was further investigated in order to determine which of the two possible isomers it was. Reduction to the corresponding amyl alcohol seemed to be the simplest way of determining the structure, but such reducing agents as zinc dust with acetic or hydrochloric acid, the zinc–copper couple in aqueous alcohol and catalytic platinum with hydrogen were without action. Sodium amalgam removed the halogen, but none of the amyl alcohol could be isolated. Oxidation of the chloro-alcohol with alkaline potassium permanganate converted it into butyric acid, but it is conceivable that both isomers (I and II) might yield butyric acid with this reagent.

The chloro-alcohol was then converted by thionyl chloride into a dichloropentane. This latter compound reacted slowly with sodium iodide in acetone solution to liberate free iodine. This behavior, as van Duin[5] has shown, indicates that the halogens in the dichloropentane were on adjacent carbon atoms and that the chloro-amyl alcohol in question has the structure II. Finally, 1,2-dichloropentane was prepared by the addition of chlorine to pentene-1. The dichloropentane prepared from the chloro-amyl alcohol was identical with the 1,2-dichloropentane prepared from pentene-1.

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[4] Delaby, *Compt. rend.,* **176, 1153 (1923); Ann. *chim.,* 20, 56 (1923).**

[5] **Van** Duin, *Rec. trav. chim.,* **43, 341 (1924).**

These results leave no doubt that Iozitsch's observations, rather than those of Fourneau and Tiffeneau, on the products of the reaction between epichlorohydrin and ethyl magnesium bromide were correct and that the particular chloro-amyl alcohol which is formed is 1-chloropentanol-2.

Various reaction conditions were tried in an effort to find the optimum conditions for the formation of the chloro-alcohol, but the maximum yield which it was possible to obtain amounted to only 19% of the theoretical. The remainder of the reaction product was the glycerol chlorobromohydrin mentioned above. With ethylmagnesium chloride approximately the same amounts of the chloro-alcohol along with a corresponding quantity of the glycerol dichlorohydrin were obtained.

Experimental

I–Chloropentanol-2.—The following procedure was found to give the best yield of this product. A solution of ethylmagnesium bromide prepared from 109 g. (1 mole) of ethyl bromide and 26.5 g. (1.1 atom) of magnesium in 300 cc. of ether was added slowly with stirring to 92.5 g. (1 mole) of epichlorohydrin dissolved in 100 cc. of ether contained in a three-necked flask fitted with a stirrer, reflux condenser and dropping funnel. During the addition the flask was cooled with running water. The mixture was refluxed for one hour and allowed to stand for two days at room temperature, the flask being closed with a soda-lime tube. *At* the end of this time, no appreciable precipitate had formed in the reaction mixture. A solution of 75 g. of acetic acid in 200 cc. of water was then added slowly with stirring and external cooling. The ether layer was separated, washed with dilute sodium carbonate solution until neutral, and the ether distilled off on a water-bath at 60°. The remaining oil was fractionated five times under reduced pressure, fractions being taken every 5° from 70 to 105° (20 mm.). The total weight of these fractions was 135–140 g. The fractions boiling to 85° were refractionated three times at atmospheric pressure, the part boiling at 157–160° (735 mm.) being practically pure chloropentanol; yield, 20–23 g. (16–197, of the theoretical); d_{25}^{25} 1.0143; n_{D}^{25} 1.4404.

Anal. Calcd. for $C_5H_{11}OCl$: Cl, 28.9. Found: Cl, 28.7.

The following variations in the preparation were tried. (a) After the reactants had been mixed, the ether was distilled off and simultaneously replaced by higher-boiling inert solvents such as benzene and toluene. There was no appreciable precipitate formed in the benzene (or toluene) solution even after four to five hours of refluxing. When the reaction mixture was fractionated, the boiling point range of the product indicated that only a small amount of chloro-alcohol had been formed. (b) After the reactants had been mixed, the ether was distilled off and the dry addition product was heated on a water-bath.[6] This treatment caused the rearrangement to take place with explosive violence, and a carbonaceous, ash-like mass was left from which none of the chloro-alcohol could be isolated. (c) The reactants were mixed and allowed to stand for two weeks in ether. After about three days, a white precipitate settled out of the solution. On longer standing, an inflammable gas, which analysis showed to be a mixture of ethylene, ethane and hydrogen, was given off from the reaction mixture. Only 6.5 g of chloro-amyl alcohol was obtained when the reaction mixture was worked up in the usual way. (d) n-Butyl ether was used as a solvent instead of ordinary ethyl ether, and the reactants were heated at various temperatures up to the boiling point

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[6] *Cf.* Grignard Bull. *soc. chim.,* **[3]** 29, 944 (1903).

of the solvent (140°). By these procedures it was not possible to isolate any of the chloro-alcohol. It was apparent, however, that some fundamental change had occurred in the reaction mixture, for when the reactants were mixed in butyl ether, a white crystalline precipitate formed which on further heating changed into a brown, porous, brittle mass from which not even the glycerol chlorobromohydrin could be isolated. If the initial precipitate from the butyl ether was hydrolyzed immediately, glycerol chlorobromohydrin was the only product obtained.

Acetate of I-Chloropentanol-2.—Ten grams of the chloro-alcohol was warmed with an equal weight of acetyl chloride on the water-bath until no more hydrogen chloride was given off. Water was then added, the oil washed with dilute sodium carbonate solution and dried over calcium chloride. The acetate distilled at 186–188° (740 mm.); d_{25}^{25} 1.0825; n_{D}^{25} 1.4328.

Anal. Calcd. for $C_7H_{13}O_2Cl$: Cl, 21.2. Found: Cl, 21.1.

3,5-Dinitrobenzoate of 1-Chloropentanol-2.—A mixture of 2.5 g. of the chloro-alcohol and 4.61 g. of 3,5-dinitrobenzoyl chloride was heated on an oil-bath to 135° until no more hydrogen chloride was given off. The sirupy brown liquid was dissolved in hot alcohol and on cooling the ester crystallized out in colorless plates which melted after another recrystallization from alcohol at 83–84°.

Anal. Calcd. for $C_{12}H_{13}O_6N_2Cl$: Cl, 11.3. Found: Cl, 11.5.

To a solution of 11 g. of potassium permanganate in 100 cc. of water was added 2.5 g. of 1-chloropentanol-2 and the solution refluxed until the permanganate color was destroyed. The manganese dioxide was then filtered off and the filtrate acidified with sulfuric acid and distilled. The distillate, after neutralization with sodium hydroxide, was evaporated to dryness. The resulting sodium butyrate was converted into the *p*-toluidide of the acid, which after recrystallization melted at 70–72°.

1,2-Dichloropentane from I-Chloropentanol-2.—Twelve grams of the alcohol was mixed with 15 g. of freshly distilled diethylaniline in a flask fitted with a reflux condenser. The mixture was cooled while 24 g. of thionyl chloride was added through a dropping funnel.[7] The mixture solidified and became brown during the addition, but it liquefied when all of the thionyl chloride had been added. The reaction was completed by heating on the water-bath until the evolution of sulfur dioxide had ceased. Water was added and the oil steam distilled out. After washing with concd. sulfuric acid and then sodium carbonate solution, and drying with calcium chloride, the oil was fractionated. The yield was 9.6 g. of a product boiling at 145.8–146.2° (739 mm.); d_{25}^{25} 1.0767; n_{D}^{25} 1.4448.

Anal. Calcd. for $C_5H_{10}Cl_2$: Cl, 50.3. Found: Cl, 50.1.

To a solution of 15 g. of dry sodium iodide in 100 cc. of dry acetone was added 5 g. of the dichloropentane as obtained above. The solution was refluxed for about six hours, after which time the solution was distinctly colored with free iodine and a precipitate of about 1 g. of sodium chloride had formed. The acetone was distilled off and water added to the residue. The insoluble oil was taken up in ether, washed with sodium thiosulfate, dried, and after removal of the ether, distilled. The dichloropentane that was recovered amounted to 3.2 g.

1,2-Dichloropentane from **Pentene-1.**—Pentene-1 was prepared according to the method of Kirrmann.[8] Seven grams of pentene-1 was dissolved in 50 cc. of carbon tetrachloride. The solution was cooled with ice and chlorine was passed in under diffused artificial light until the yellow color remained in the solution for about thirty seconds after the current of chlorine had been stopped. After the removal of the carbon tetra-

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[7] Cf. Darzens, *Compt. rend.*, 152, 1314 (1911).

[8] Kirrmann, *Bull. soc. chim.*, **39**, 988 (1926).

chloride from the product by fractional distillation, the dichloropentane distilled at 146.0–146.2"; yield, 7 g.; d_{25}^{25} 1.0773; n_D^{25} 1.4453.

Anal. Calcd. for $C_5H_{10}Cl_2$: Cl, 50.3. Found: Cl, 49.8.

1-Chloro-3-Bromopropanol-2.—The fraction boiling at 100–105° (20 mm.) from the preparation of 1-chloropentanol-2 was refractionated under reduced pressure into a part boiling at 95–98° (15 mm.) which was the glycerol chlorobromohydrin described by Fourneau and Tiffeneau.[3] The compound was colorless when freshly distilled but darkened rapidly on exposure to light. It boiled with much decomposition at 190–200° (740 mm.), and for this reason was best purified by distillation under diminished pressure; d_{25}^{25} 1.7456; n_D^{25} 1.5140.

Anal. Calcd. for C_3H_6OClBr: Cl, 20.4; Br, 46.1. Found: Cl, 20.1; Br, 45.3.

No effort was made to secure the maximum yield of this compound. Presumably, however, about 100 g. of it was available from a run of one mole of epichlorohydrin, since the total weight of reaction product was about 140 g. and about 23 g. of chloropentanol was obtained from this. The intermediate fractions weighed 10–15 g.

The chlorobromohydrin was further identified by preparing the known 1,3-diphenoxypropanol-2 from it by the procedure described by Rossing[9] for the preparation of this substance from a-dichlorohydrin. The melting point of the diphenoxy compound after recrystallization from alcohol was 80–81°.

Summary

1. It has been shown that ethylmagnesium bromide reacts with epichlorohydrin to give a chloro-amyl alcohol as well as glycerol chlorobromohydrin.

2. The chloro-amyl alcohol which is formed has been found to be 1-chloropentanol-2.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE POLYTECHNIC INSTITUTE]

STUDIES ON HYDRAZINE. THE HYDROLYSIS OF DIMETHYLKETAZINE AND THE EQUILIBRIUM BETWEEN HYDRAZINE AND ACETONE

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One of the most important properties of hydrazine and its organic substitution products is their capacity to react with the carbonyl group of ketones and aldehydes, forming hydrazones or azines by elimination of water. This reaction takes place most generally in neutral or alkaline solution, while in acid the product is to a greater or less extent, depending on the particular componenis, hydrolyzed. A study of this type of hydrolysis, using the product formed in the reaction of hydrazine with the simplest ketone, acetone, has been made in the work here presented.

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[9] Rossing, ***Ber.,*** 19, 64 (1886).

[1] Fellow of the John Simon Guggenheim Memorial Foundation.

When hydrazine and acetone are brought together under the proper conditions, two molecules of acetone combine with one of hydrazine to form dimethylketazine.[2] This ketazine dissolves readily in water and the solution becomes alkaline. If the free hydroxyl ion is neutralized with acid, more OH^- is then formed. In the presence of strong mineral acids the compound is completely hydrolyzed. The hydrolysis takes place with measurable velocity and the progress of the reaction may be followed by measuring the amount of acid necessary to replace the H^+ which has reacted with the ketazine, adding the acid at such a rate as to maintain a constant PH in the solution. Examination of the reaction, however, showed the probability of there being present also acetone hydrazone, containing one molecule of acetone and one of hydrazine. In addition to this the reaction proved to be highly reversible, coming to equilibrium at PH 5.0 when from 30 to 70% of the ketazine had been hydrolyzed, the extent depending not only on the PH but also on the original concentration of ketazine.

The entire reaction may be formulated, therefore, either as a reaction between dimethylketazine and water to form the acetone hydrazone, which is in turn hydrolyzed to hydrazine and acetone, or as a direct hydrolysis of the ketazine to acetone and hydrazine, with the hydrazone formed by a side reaction between the two latter. The equations are

$$\underset{C}{(CH_3)_2C{=}N{-}N{=}C(CH_3)_2} + H^+ + H_2O \rightleftharpoons \underset{D}{(CH_3)_2C{=}N{-}NH_3^+} + \underset{B}{(CH_3)_2CO} \quad (1)$$

followed by

$$\underset{D}{(CH_3)_2C{=}N{-}NH_3^+} + H_2O \rightleftharpoons \underset{A}{N_2H_5^+} + \underset{B}{(CH_3)_2CO} \quad (2)$$

or, alternatively

$$\underset{C}{(CH_3)_2C{=}N{-}N{=}C(CH_3)_2} + H^+ + 2H_2O \rightleftharpoons \underset{A}{N_2H_5^+} + \underset{B}{2(CH_3)_2CO} \quad (1a)$$

and

$$\underset{A}{N_2H_5^+} + \underset{B}{(CH_3)_2CO} \rightleftharpoons \underset{D}{(CH_3)_2C{=}N{-}NH_3^+} + H_2O \quad (2a)$$

Denoting by subscripts the equations for which the equilibrium constants are valid, the following relations exist

$$K_1 \times K_2 = K_{1a} \text{ and } K_{2a} = 1/K_2$$

The problem may therefore be resolved into three parts: (1) to determine the conditions of Equilibrium 2 or 2a; (2) to determine the conditions of Equilibrium 1 or 1a; (3) to study the kinetics of the hydrolysis. These will be taken up in the order named.

Part I

The Equilibrium between Acetone, Nydrazine and Acetone Hydrazone.—Since Reaction 1 or 1a involves H^+ on the left-hand side of the

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[2] Curtius and Thun, *J. prakt. Chem.*, 44, 164 (1891).

equation, it is evident that by adding sufficient acid this equilibrium may be shifted completely to the right, while 2 or 2a will be unaffected by acid and may thus be studied independently. This was done by two different procedures.

1A. Determination of Equilibrium 2a by Solubility Measurements.—It has previously been found that hydrazine picrate[3] is an easily prepared salt sufficiently insoluble to be suited for measurements of solubility. The salt moreover contains only one equivalent of acid for each molecule of hydrazine, *i. e.*, it contains the ion $N_2H_5^+$. By measuring the increase in solubility of the salt when acetone is added to the solvent, the equilibrium between acetone, hydrazine and acetone hydrazone readily may be determined. The acidity must be adjusted so that no dimethylketazine is formed. The thermodynamic mass action law applied to Equation 2a yields the expression

$$K_{2a} = \frac{C_{\text{acetone hydrazone}^+}}{C_{N_2H_5^+} \times C_{\text{acetone}}} \times \frac{\mathbf{fl}}{f_1 \times f_0} \tag{3}$$

where f_1 stands for the activity coefficients of the two monovalent ions and f_0 for that of acetone. At low concentrations this factor would be of little import, but some salt effect upon the equilibrium would be expected at higher concentration. It has been shown,[4] however, that in solutions of sufficiently high ionic strength the activity coefficient factor may be neglected and concentration values employed directly in the mass action law and it was thought best to employ this expedient rather than introduce the activity coefficients.

TABLE I

SOLUBILITY OF HYDRAZINE PICRATE AND EQUILIBRIUM WITH ACETONE AT 15°

Solvent 0.2 M NaCl + 0.02 M HCl + acetone

(a) Solubility

Orig. concn. of acetone	Total hydrazine	Orig. concn. of acetone	Total hydrazine	Orig. concn. of acetone	Total hydrazine
0	0.01480	0.04388	0.01745	0.09654	0.02102
0	.01476	.06582	.01871	.1097	.02198
0	.01480	.07898	.01985	.1097	.02211
0.0392	.01712	.07679	.01980	.1097	.02211
.0400	.01715	.08776	.02030	.09404	.02082
.05485	.01813	.09524	.02113	.1097	.02181
.05480	.01803	.09873	.02122	.1097	.02211

(b) Equilibrium Data

B_0 acetone	Total Pic.⁻ (A + D)	$K_{\text{s p.}} \times 10^4$	A	D	B	K_{2a}
0.040	0.01738	2.24	0.01289	0.00449	0.03551	9.80
.070	.01921	2.28	.01184	.00737	.06263	9.92
.100	.02147	2.31	.01078	.01069	.08931	11.1
					Mean	10.3

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[3] Gilbert, *J. Phys. Chem.*, **33**, 1235 (1929).

[4] Bronsted, *Z. physik. Chem.*, **102**, 169 (1922); Bronsted and Pedersen, *ibid.*, 103, 307 (1922).

The solubility of hydrazine picrate was therefore determined at 15° in the presence of acetone, 0.2 M sodium chloride and 0.02 M hydrochloric acid (the latter to prevent formation of dimethylketazine). Results are given in Table I. These were further confirmed by measurements in acetone, 0.2 M sodium chloride, and 0.01 *M* hydrochloric acid, Table II; in acetone and 0.04 *M* picric acid, Table III; and finally in acetone, 0.133 *M* sodium chloride, 0.067 M sodium picrate and 0.0033 *M* hydrochloric acid, Table IV.

TABLE II

SOLUBILITY OF HYDRAZINE PICRATE AND EQUILIBRIUM WITH ACETONE AT 15°

Solvent: 0.2 M NaCl–0.01 *M* HCl–acetone

(a) Solubility

Original acetone concn.	0	0	0.05485	0.1097	0
Total hydrazine	0.01443	0.01447	0.01799	0.02177	0.01443

(b) Equilibrium Data

Ro, acetone	Total Pic.– (*A* + *D*)	$K_{s \cdot p}$ X 104	A	D	*B*	K_{2a}
0.040	0.01702	2 13	0.01245	0.00457	0.03543	10.38
.070	.01896	2.17	.01145	.00751	.06249	10.50
.100	.02107	2.20	.01045	.01062	.08938	11.35
					Mean	10.74

TABLE III

SOLUBILITY OF HYDRAZINE PICRATE AND EQUILIBRIUM WITH ACETONE AT 15°

Solvent: 0.04 *M* Picric acid–acetone

(a) Solubility

Orig. acetone concn.	0	0	0.0439	0.0658	0.0878	0.1097	0.1097
Total hydrazine	0.00448	0.00448	0.00630	0.00687	0.00826	0.00938	0.00943

(b) Equilibrium Data

B_0 acetone	*A* + *D*	Total pic.⁻	$K_{s\,p}$ X 104	*A*	*D*	*B*	K_{2a}
0.040	0.00607	0.0461	2.05	0.00445	0.00162	0.03738	9.74
.070	.00738	.0474	2.08	,00438	.00300	.06700	10.23
.100	.00887	.0489	2.10	.00430	.00457	.09543	11.10
						Mean	10.3

TABLE IV

SOLUBILITY OF HYDRAZINE PICRATE AND EQUILIBRIUM WITH ACETONE AT 15°

Solvent: 0.1333 M NaCl-0.0667 NaPic–0.003 M HCl–acetone

(a) Solubility

Original acetone concentration	0	0.05485	0.1080
Total hydrazine	0.00420	0.00677	0.00933

(b) Equilibrium Data

B_0, acetone	*A* + D	Total pic.⁻	$K_{s\,p}$ × 104	*A*	*D*	*B*	K_{2a}	K_{2a} corr.
0.05485	0.00677	0.07344	3.03	0.00413	0.00264	0.0559	11.44	10.9
.1080	.00933	.07600	3.07	.00404	0.00529	0.1027	12.75	11.6

(a) Materials.—Hydrazine picrate was prepared as previously described and rotated in water at 15° until succeeding samples of the solution gave the same value for the solubility. This material was used for subsequent determinations. Acetone was the best product obtainable, "zur Analyse," and was twice redistilled. A stock solution was made by weighing acetone in sealed ampules and breaking these under the surface of water in a volumetric flask.

(b) **Procedure.**—Solutions to be used as solvents for the hydrazine picrate were made by dilution of stronger stock solutions to give the desired concentration of each reagent. Care was taken to minimize loss of acetone by volatilization. Solubility measurements were made for the most part in sealed tubes. Some of the later ones were made in well stoppered bottles. In a few cases to serve as a check against volatilization losses, small weighed ampules of acetone were broken in the solubility bottle after closing it. All of the methods gave concordant results. Hydrazine was determined by the iodic acid method.[5] Previous tests had shown that picric acid does not interfere with this method.[3]

It was necessary to remove acetone. This was done by acidifying the solution and boiling for several minutes to decompose acetone hydrazone and drive off the acetone. Tests were made to prove the efficacy of this procedure. Additional tests were made to ensure that acetone did not have a solvent effect additional to that caused by reaction with hydrazine. This was done,by determination of the solubility of a similar salt, potassium picrate, in 0.2 M sodium chloride and then in 0.2 M sodium chloride plus 0.1 M acetone. No increase in solubility was found in the acetone solvent.

(c) Calculations.—The values of the solubility were plotted on a large scale and a curve was drawn through the points. Interpolated values were taken from this for the calculations. Since acetone hydrazone is decomposed by boiling before titration, the concentration of hydrazine found by titration represents the sum of the $N_2H_5^+$ (A) and the acetone hydrazone (D) and therefore also the concentration of the picrate ion (Pic.–). The concentration *(A)* at equilibrium is found by dividing the solubility product of hydrazine picrate by (Pic.–). Acetone hydrazone (D) is then obtained by subtracting *(A)* from the total hydrazine *(A* + D) found by titration. The acetone concentration (B) is equal to the original concentration of acetone in the solvent, minus (D).

In solutions which contain added sodium picrate or picric acid (in the solvent) allowance must be made for this in determining $K_{\text{s.p.}}/\text{Pic.}^- = N_2H_5^+ = (A)$. Furthermore, our earlier work has shown that small amounts of picrate ion have a marked specific effect on the solubility of picrates with the result that the solubility product increases considerably due to the additional hydrazine picrate dissolved by the acetone, even in the small range covered in these determinations of solubility. Approximate correction-was made for this increase and the $K_{\text{s.p.}}$ used in calculating is given in each case.[6]

[5] Bray and Cuy, THIS JOURNAL, 46, 858 (1924).

[6] This correction was made as follows:

at 15° $K_{\text{s.p}}$ $N_2H_5\text{Pic.}$ in 0.2 M NaCl + 0.02 M HCl = 2.19×10^{-4} (1)

at 15° $K_{\text{s.p.}}$ $N_2H_5\text{Pic.}$ in 0.2 M NaCl + 0.01 M HCl = 2.08×10^{-4} (2)

at 15° $K_{\text{s.p.}}$ $N_2H_5\text{Pic.}$ in 0.2 M NaCl = 1.99×10^{-4} (3)

by interpolation $N_2H_5\text{Pic.}$ in 0.2 M NaCl + 0.0033 M HCl = 2.01×10^{-4} (4)

$$\text{by expt. } N_2H_5\text{Pic. in } \left\{\begin{matrix} 0.133\ M\ \text{NaCl} \\ 0.067\ M\ \text{NaPic.} \end{matrix}\right\} + 0.0033\ M\ \text{HCl} = 2.98 \times 10^{-4} \qquad (5)$$

From (4) and (5) it may be seen that changing Pic.$^-$ from 0.0709 to 0.0142 M causes

The values of the equilibrium constant calculated from measurements in *0.0033 M* hydrochloric acid were rather high (Table IV), but when the constant for the equilibrium between hydrazine, acetone and dimethylketazine was determined (Part 2) it was seen that this acid concentration is so low that appreciable amounts of ketazine were present, in addition to the acetone hydrazone. When allowance was made for this, much better agreement was obtained, as noted in the "corrected K," Table IV.

1B. Determination of Equilibrium **2a from Distribution Experiments.**—Mainly as a check on the solubility method the equilibrium was determined also by the distribution of acetone between benzene and solutions containing 0.2 M sodium chloride and 0.02 M hydrochloric acid, without and with addition of hydrazine hydrochloride. Knowing the distribution ratio when no hydrazine was present, the amount of free acetone in the equilibrium solution when hydrazine is present readily may be calculated. The difference gives the amount which has combined to form acetone hydrazone. The results are summarized in Table V.

TABLE V

EQUILIBRIUM FROM DISTRIBUTION OF ACETONE BETWEEN BENZENE AND HYDRAZINE HYDROCHLORIDE SOLUTIONS

Solvent: 0.2 M $NaCl$–0.02 M HCl with or without 0.02 M N_2H_5Cl

Concn. acetone in water layer, with no N_2H_5 present	Concn. acetone in water layer with 0.02 M N_2H_5Cl	*A*	*D*	K_{2a}
0.0593	0.0510	0.0117	0.0083	(13.9)
.0297	.0260	.0163	.0037	8.74
.0297	.0262	.0165	.0035	8.10
.0593	.0513	.0120	.0080	(13.0)
.0297	.0258	.0161	.0039	9.4

(a) Procedure.—The strong stock solutions were diluted to give the proper concentration of each reagent and 50 cc. each of benzene and the solution were rotated together for eighteen hours at 15°. Fifteen cc. samples were then taken and the acetone in the benzene layer was determined by Messinger's method.[7]

The validity of the distribution method depends upon the assumption that no hydrazine or acetone hydrazone passes into the benzene layer. Since the solution is acid, both should be present as salts. There is reason to believe that the salts would be little soluble in benzene but several benzene samples were carefully tested for the presence of hydrazine after boiling with *3* M acid. The results were entirely negative, proving the absence of hydrazine, hydrazone and ketazine from the benzene layer. The high solubility of acetone in benzene reduced the available concen-

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a change of 0.97 X 10^{-4} in the $K_{s.p.}$. It was assumed that this increase would be linear and that smaller changes in Pic.– such as would be met when acetone is added to the solvent (increasing the solubility) would cause a proportional change.

[7] Goodwin, THIS JOURNAL, 42, 39 (1920).

tration in the water layer so much that small errors are magnified in obtaining the equilibrium data, but the results give good confirmation for the solubility measurements.

The mean value of K_{2a} from all the experiments, both solubility and distribution, is 10.3, but in view of the uncertainty regarding salt effects which may exist it is reasonable to round it off to 10.0. This will be used in the subsequent calculations.

Having thus established the relation existing between acetone, hydrazine and acetone hydrazone, it is possible to determine the hydrolysis equilibrium of dimethylketazine.

Part II

Determination of the Equilibrium Constant for the Hydrolysis of **Dimethylketazine.**—The hydrolysis was studied with the use of a device previously described,[8] by which the investigators followed the addition of anions to the ethylene oxides. The essential part consisted of a microburet with a very fine tip from which acid was run into the solution at a rate just sufficient to replace the H^+ used in the hydrolysis of the ketazine. The previous reaction differed from the present in that it was independent of the hydrogen-ion concentration, while in our work the hydrogen ion was one of the reactants. It was necessary therefore to have a much closer regulation of the PH in this case.

(a) Procedure.—The vessel containing the ketazine solution was placed in a narrow, transparent, constant-temperature bath and sky light reflected through it. A suitable amount of indicator (brom cresol green) was placed in the reacting solution, and in similar vessels on each side were placed, with the same amount of indicator, phthalate buffer solutions differing by 0.1 *PH* unit (greater and less) from the *PH* desired for the equilibrium mixture. A mechanical stirrer was provided, operating through a stopper, and acid (0 8089 M) was run in from the buret at a rate to keep the color of the indicator within the limits set by the standards on either side. The readings of the buret were taken from time to time and they furnished a record of the velocity of the reaction for Part **3.** The final reading was taken after a matter of hours in order to ensure attainment of equilibrium. It would appear that the best results one might hope for would be not closer than 0.1 *PH* unit, but by working only when the light was good much better results than this were actually realizable, as the curves show.

(b) Results.—Equilibrium data were obtained at 15° over a range of ketazine concentration from 0.007 to 0.037 M at *PH* 5.35 and 4.95;[9] at *PH* 5.00 and 4.60 with M sodium chloride as solvent instead of water, and, finally, at 20°, at *PH* 5.35, using in all cases brom cresol green as indicator. The reacting solution had a volume of 51 cc. (50 in a few runs) to which were added during the reaction varying amounts of perchloric acid—never more than 1.10 cc. This was corrected for in calculating the

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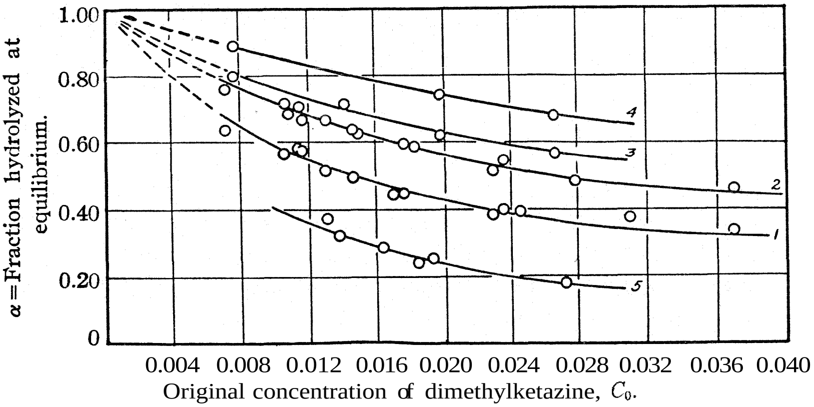
[8] Bronsted, Kilpatrick and Kilpatrick, THIS JOURNAL, 51, 428 (1929).

[9] These *PH* values have been corrected as suggested by Koltlioff. J. Phys. *Chem.*, **32,** 1820 (1928), for differences between reacting salt concentration and the concentration of the standard buffers.

constants. In Fig. 1 there is plotted as ordinate the fraction "α" of dimethylketazine which has been hydrolyzed at equilibrium; as abscissa the total concentration of ketazine, hydrazine and acetone hydrazone. This was determined by boiling a measured sample of the equilibrium mixture with dilute acid to decompose the acetone compounds and volatilize the acetone, and then titrating the hydrazine. This gives C_0, the original concentration of ketazine with allowance made for dilution by the added acid. For the sake of economy of space not all the data for Fig. 1 are included but Table VI gives typical results, together with the percentage deviation of the individual points from the smooth curve. For only one point in Fig. 1 is the deviation greater than 5%. Since by our device



1, *Ph* 5.35, temp., 15°; 2, *Ph* 4.95, temp., 15°; 3, *Ph* 5.00, temp., 15°, 1.0 M NaCl; 4, *Ph* 4.60, temp., 15°, 1.0 M NaCl; 5, *Ph* 5.35, temp., 20°, add 0.30 to ordinates.

Fig. 1.—Variation of hydrolysis equilibrium with concentration of ketazine,

TABLE VI

TYPICAL EXPERIMENTAL POINTS FOR EQUILIBRIUM CURVES IN FIG. 1

(a) Temp., 15°; *Ph*, 4.95 (curve 2)

Orig. concn. of ketazine, C_0	Fraction reacted at equilibrium	Curve	Deviation, %	Orig. concn. of ketazine, C_0	Fraction reacted at equilibrium	Curve	Deviation, %
0.007	0.752	0.784	−4.0	0.02346	0.548	0.526	+4.2
.01054	.714	.700	+2.0	.02780	.481	.493	− 2.3
.01073	.683	.695	−1.7	.03697	,460	.448	+2.7
.01125	.717	.688	+4.2				
.01144	.688	.673	−0.7	(b) Temp., 20°; *Ph*, 5.35 (Curve 5)			
.01290	.664	.657	+1.1	.01300	.672	.642	+4.7
.01482	.626	.642	−2.5	.01375	.620	.628	−1.3
.01450	.638	.632	+1.0	.01624	.597	.598	...
.01756	.594	.588	+1.0	.01840	.540	.558	−3.2
.01820	.588	.580	+1.6	.01923	.553	.549	+0.7
.02285	.514	.531	−3.2	.02730	.530	.536	−1.1

the H^+ is kept constant during any series of runs, the reaction becomes essentially monomolecular to the right (see Equations 1 and 1a), and bi- or trimolecular in the reverse direction. Dilution will thus favor the hydrolysis, and as C_0 approaches zero, α will approach 1.0. This fact was taken into consideration in drawing the best curve for each set of points.

(c) Calculations.—For the calculation of the hydrolysis equilibrium there were in each case four quantities available: (1) C_{H^+}, which was constant and used only in the final calculation (ordinarily it was included with the constant); (2) the sum of the equilibrium concentrations of ketazine, acetone hydrazone and hydrazine (C + D + A) (This is equal to C_0, the total ketazine if no hydrolysis had taken place.) **(3)** the concentration of acid needed to bring the system to equilibrium at the desired PH. (This is equal to the concentration of the hydrazine plus that of acetone hydrazone (D + A) and also equal to αC_0 = amount of ketazine hydrolyzed); (4) the equilibrium constant, K_{2a}, which fixes the relation between acetone, hydrazine and acetone hydrazone.

$$K_{2a} = \frac{D}{A \times B} = 10.0 \text{ or } \frac{A \times B}{D} = 0.1 \tag{4a}$$

With these at hand calculation was made as follows: Equations 1 and 2 show that if neither hydrazine nor acetone is added from without

$$\text{the concentration (B) of acetone at equilibrium} = 2A + D \tag{6}$$

for if A = 0, B = D; if D = 0, B = 2A. Then

$$\frac{A \times (2A + D)}{D} = 0.1 \tag{4a}$$

but

$$A + D = \alpha C_0 \text{ and } D = (\alpha C_0 - A) \tag{7}$$

Substituting this value for D in (4a) and solving

$$N_2H_5^+ = A = \frac{-(\alpha C_0 + 0.1) + \sqrt{(\alpha C_0 + 0.1)^2 + 0.4\alpha C_0}}{2} \tag{8}$$

Using (8), (7) and (6), the quantities needed for the calculation of K_1 or K_{1a} may be obtained from the two experimental figures C_0 and α.[10]

The constant so obtained contains in it the constant factor C_{H^+}. Introducing a numerical value for C_{H^+} gives a value for K_{1a} which may be used for the calculation of the hydrolysis under any desired condition of acidity. Table VII gives the results at different PH and temperatures. They may be summarized as indicated in Table VIII.

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[10] The concentration of acid added will only be equal to that of the hydrazine and hydrazone formed by hydrolysis if the unhydrolyzed ketazine itself does not act as a base. To test this, acetone was added to dimethylketazine, with a small amount of water. This served to prevent hydrolysis of the ketazine. When no indicators were added to the solution, it was found to be slightly acid to brom thymol blue, slightly basic to brom cresol green, and neutral to brom cresol purple, showing that the ketazine itself does not, under these conditions at least, function as a base.

TABLE VII

EQUILIBRIUM CONSTANT FOR HYDROLYSIS OF DIMETHYLKETAZINE, K_{1a}

(a) PH, 5.00; temp., 15°; solvent 1 M NaCl

C_0	$C = (1 - \alpha)C_0$	$A + D$	A	D	$B = 2A + D$	$K_{1a}\,C_{H^+} \times 10^4$	
0.007	0.001319	0.005681	0.00510	0.00058	0.01078	4.5	
.010	.00240	.00760	.00665	.00095	.01425	5.6	
.015	.00465	.01035	.00870	.00165	.01905	6.8	
.020	.00748	.01252	.01020	.00232	.02272	7.1	
.025	.01050	.01450	.01155	.00295	.02605	7.5	
.030	.01374	.01626	.01265	.00361	.02891	7.6	Mean 6.93

(b) PH, 5.35; temp., 15°; solvent, H_2O

C_0	$C = (1 - \alpha)C_0$	$A + D$	A	D	$B = 2A + D$	$K_{1a}\,C_{H^+} \times 10^4$	
0.007	0.002294	0.004706	0.00432	0.000394	0.00903	1.6	
.010	.00412	.00588	.00529	.000590	.01117	1.6	
.015	.00764	.00736	.00645	.000910	.01381	1.6	
.020	.01150	.00850	.00734	.00116	.01584	1.6	
.025	.01550	.00950	.00810	.00140	.01758	1.6	
.030	.01956	.01044	.00880	.00169	.01919	1.7	
.035	.02365	.01135	.00940	.00195	.02075	1.7	
[a]	.01724	....	.01585	.00219	.01389	1.8	
[a]	.01935	....	.01550	.00207	.01307	1.4	Mean 1.64

(c) PH, 5.35; temp., 20°; solvent, H_2O

C_0	$C = (1 - \alpha)C_0$	$A + D$	A	D	$B = 2A + D$	$K_{1a}\,C_{H^+} \times 10^4$	
0.010	0.00300	0.00700	0.0062	0.00080	0.01320	3.6	
.015	.00590	.00910	.0078	.00130	.01690	3.8	
.020	.00920	.01080	.0090	.00180	.01980	3.8	
.025	.01268	.01232	.01005	.00227	.02237	3.97	Mean **3.8**

(d) *P*H, 4.95; temp., 15°; solvent, H_2O

C_0	$C = (1 - \alpha)C_0$	$A + D$	A	D	$B = 2A + D$	$K_{1a}\,C_{H^+} \times 10^4$	
0.007	0.00150	0.005495	0.00498	0.000515	0.01047	3.6	
.010	.00288	.00712	.00630	.00082	.01342	3.9	
.015	.00564	.00936	.00802	.00134	.01738	4.3	
.020	.00880	.01120	.00930	.00190	.02051	4.4	
.025	.01215	.01285	.01045	.00240	.02331	4.6	
.030	.01560	.01440	.01145	.00295	.02580	4.9	
.035	.01911	.01589	.01239	.00350	.02829	5.2	
[a]	.01498	.02194	.01830	.00364	.02024	5.0	Mean 4.5

(e) PH, 4.60; temp., 15°; solvent, 1 *M* NaCl

C_0	$C = (1 - \alpha)C_0$	$A + D$	A	D	$B = 2A + D$	$K_{1a}\,C_{H^+} \times 10^4$	
0.007	0.00073	0.00627	0.00560	0.00067	0.01187	(10.8)	
.010	.00145	.00855	.00740	.00115	.01595	(13.0)	
.015	.00309	.01191	.00980	.00211	.02171	15.0	
.020	.00520	.01480	.01170	.00310	.02650	16.0	
.025	.00765	.01735	.01332	.00403	.03067	16.0	
.030	.01044	.01956	.01455	.00501	.03411	16.0	Mean 16.0

[a] 0.01 M N_2H_5 added before the run.

(d) Discussion.—The equilibrium may be calculated either on the basis of

$$\frac{C_{N_2H_5^+} \times C_{\text{Acetone}}^2}{C_{\text{Ketazine}}} = K_{1a}\cdot C_{H^+}, \text{ or}$$

$$\frac{C_{\text{Acetone hydrazone}^+} \times C_{\text{Acetone}}}{C_{\text{Ketazine}}} = K_1\cdot C_{H^+}$$

As seen in Table VIII the constant in the second case will be 10 times that in the first, since $K_1 = K_{1a} \cdot K_{2a} = 10K_{1a}$. Since K_{1a} deals with the final simple products of the reaction, it is perhaps preferable to K_1 and the tables have been so prepared. For some purposes K_1 is better. Thus from Table VIII we can find that in water at 15° K_1 has a mean value of 370. If now a value of 0.01 is taken for C_{H^+} and some typical results are chosen from Table II; A = 0.01245, B = 0.03543 and D = 0.00457; then C, the concentration of ketazine present, will be $(0.00457 \times 0.0345)/(C \times 0.01) = 370$; $C = 0.00004$ M. This is less than 1% of the acetone hydrazone present and may therefore be neglected in calculating K_{2a} (as in Part 1) when 0.01 M acid is present.

TABLE VIII

HYDROLYSIS CONSTANTS FOR DIMETHYLKETAZINE AT 15°

PK	Solvent	$K_1 \cdot C_{H^+}$	$K_{1a} \cdot C_{H^+}$	K_{1a}
5.35	Water	1.64×10^{-3}	1.64×10^{-4}	36.5
4.95	Water	$4.5 \times$	4.5×10^{-4}	37.5
5.00	1 *M* NaCl	6.93×10^{-3}	6.93×10^{-4}	73.8
4.60	1 M NaCl	$15.9 \times$	15.9×10^{-4}	69.3
5.35 (20°)	Water	3.8×10^{-3}	3.8×10^{-4}	84.4

On the other hand, if $C_{H^+} = 0.0033$, as in Table IV, C becomes an appreciable quantity. Using typical data

$$C = \frac{0.02264 \times 0.0559}{370 \times 0.0033} = 0.00012$$

The ketazine = $0.00012/0.00264 \times 100 = 4.5\%$ of the hydrazone present. This explains the fact that using uncorrected figures for the concentration of hydrazone in this solvent a very high value for K_{2a} is obtained. Allowance for the ketazine brings K_{2a} into agreement with the values found in the presence of stronger acid where the ketazine concentration is negligible.

A rise in temperature shifts the equilibrium greatly to the right, favoring the hydrolysis.

The use of a concentrated (1 *M*) sodium chloride solution as solvent gives a large positive salt effect on the equilibrium constant, the value being approximately double what it is in the solutions of low ionic strength. Writing the equilibrium

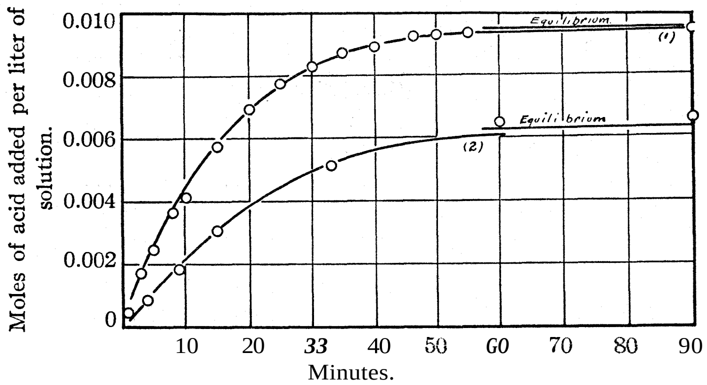
$$K_{18} = \frac{C_{N_2H_5^+} \times C_{Acetone}^2}{C_{Ketazine} \times C_{H^+}} \times \frac{f_1 f_0^2}{f_0 f_1}$$

it is seen that in quite dilute solution there will be approximate equality between f_1 in the numerator and f_1 of H^+ in the denominator; likewise between the activity coefficient of the acetone and ketazine, so the factor reduces to f_0, simply. These assumptions will not hold in such a strong solution as 1 M and the calculation of salt effect would be difficult.

Finally, inspection of the tables shows that at low acidity such as used in this work there is in all cases sufficient of both hydrazine and acetone hydrazone present so that neither may be neglected. All of the equilibria must be taken into account simultaneously. Having thus established the conditions of equilibrium it is possible to study the kinetics of the reaction.

Part III

The Kinetics of the Hydrolysis of Dimethylketazine.—This hydrolysis is representative of a large group of reactions where H^+ or OH– is taken up at a measurable rate. The method as used here is applicable only in cases where the PH may be kept low enough for the proper functioning of indicators, but where applicable gives a valuable method of approach as it effects a considerable simplification of the kinetics.



1, at 20°; 2, at 15°. Note: Run 2 went past the equilibrium point. The curve was drawn below the last two points, but tangent to equilibrium line. This is necessary since the mean K_E is used in the calculation.

Fig. 2.—Velocity of hydrolysis of dimethylketazine at *P*H **5.35.**

(a) Procedure.—The rate of hydrolysis was followed by reading at intervals from the buret (as in Part 2) the amount of acid which had been added. At PH 5.35 the rate was such that it could be readily followed both at 15 and at 20°. The buret was calibrated and a graph constructed by which readings could be translated into cubic centimeters, and thence to moles of acid per liter of solution.

(b) Results.—In Fig. 2 the concentration of acid added, in moles per liter, is plotted as ordinate against time for two representative runs. The data are given in Tables IX and X. Constants were calculated at points read from the curves.

(c) **Calculations.**—C_H^+ is maintained constant during the reaction and the hydrolysis will proceed as a first-order reaction opposed by a bimolecular reaction (Equation 1), or by a trimolecular reaction (Equation 1a). Since the data are interdependent and both reactions are represented in the final state of equilibrium, the kinetics will give no indication and the data will fit both assumptions.

TABLE IX

EXPERIMENTAL DATA AND CALCULATION FOR VELOCITY CONSTANT AT 15°; PH, 5.35

Time, minutes	Buret reading	Moles $HClO_4$ added to 50 cc. of reacting soln. (Buret reading X $\frac{1.022}{20} \times \frac{0.8089}{1000}$)
0	0	
1	0.52	0.0000215
4	1.00	.0000415
9	2.20	.0000913
16	3.92	.0001625
33	6.18	.0002560
60	7.90	.0003275
85	8.10	.0003351
91	8.30	.0003440

Calculation

Time	αC_0, mole/liter	$(1 - \alpha)C_0$	$\frac{d\alpha C_0}{dt}$ X 104	A	B	k_2
0	0	0.01145	..	....	....	...
5	0.00116	.01029	2.21	0.00113	0.00229	131.2
10	.00238	.00907	1.95	.00227	.00464	135.0
15	.00308	.00837	1.67	.00291	.00599	131.8
20	.00385	.00760	1.37	.00358	.00743	130.7
25	.00450	.00695	1.19	.00412	.00862	142.7
30	.00500	.00645	0.88	.00457	.00957	137.5
35	.00540	.00605	.63	.00490	.01030	137.0
					Mean	135.0

$k_1 = K_{1a} \cdot k_2 = 0.000164 \times 135.0 = 0.0221/C_H$.

TABLE X

EXPERIMENTAL DATA AND CALCULATION FOR VELOCITY CONSTANT AT 20°; *P*H, 5.35

Time, minutes	Buret reading	Moles $HClO_4$ added to 50 cc. of reacting soln. (Buret reading X $\frac{1.022}{20} \times \frac{0.5395}{1000}$)
0	0	.....
3	3.10	0.000086
5	4.45	.000124
8	6.52	.000182
10	7.40	.000206
15	10.40	.000289
20	12.50	.000347
25	14.00	.000389
30	14.92	.000415
35	15.80	.000439
40	16.10	.000448
47.5	16.60	.000462
50	16.80	.000467
55	16.85	.000468
90	17.10	.000476

TABLE X (Concluded)

Calculation

Time	αC_0 mole/liter	$(1-\alpha)C_0$	$\frac{d(\alpha C_0)}{dt} \times 10^4$	A	B	k_2
0	0	0.01614	..	.....	....	...
10	0.00432	.01182	3.19	0.00410	0.00842	74.0
16	,00600	.01014	2.43	.00540	.01140	77.0
25	.00774	.00840	1.45	.00668	.01442	81.0
35	.00874	.00740	0.69	.00747	.01621	81.0
					Mean	78.0

$k_1 = K_{1a} \cdot k_2 = 0.000380$ X $78.0 = 0.0294/C_H$.

As pointed out in Part 2, the buret reading at time "t" gives $A + D = \alpha C_0$; acetone concentration $(B) = 2A + D$, and

$$A = \frac{-(\alpha C_0 + 0.1) + \sqrt{(\alpha C_0 + 0.1)^2 + 0.4\alpha C_0}}{2}$$

Final titration of a sample for total hydrazine present gives C_0 and $C = (1 - \alpha)C_0$. Then

$$\frac{d(\alpha C_0)}{dt} = k_1(C_0 - \alpha C_0)C_{H^+} - k_2 \cdot A \cdot B^2 \tag{9}$$

or

$$\frac{d(\alpha C_0)}{dt} = k_1(C_0 - \alpha C_0)C_{H^+} - k_2' \cdot B \cdot D \tag{10}$$

Since the values of A, B and D are all expressed in terms of αC_0, the equation becomes awkward to treat analytically and the purpose is well served by a graphical solution: $K_{1a} = k_1/k_2$ in (9), while in (10) $K_1 = k_1/k_2'$.

For the reason given in Part 2, K_{1a} and Equation 9 have been employed in calculations. The final result is the same in either case.[11] Substituting

[11] It has been suggested by the reviewer that since the expression $K_{1a} = k_1/k_2' = (A)(B^2)/(C)(H^+)$ may also be stated $K_{1a} = k_1'/k_2' = \frac{(A)(B)}{(C)(H^+)/(B)}$ the velocity may be expressed by the equation (using the alphabetical symbols adopted in the paper)

$$-d(C)/dt = k_1'(C)(H^+)/(B) - k_2'(A)(B) \tag{x}$$

as distinct from the one actually used, which was based on Equation 9, *i. e.*

$$-d(C)/dt = k_1(C)(H^+) - k_2(A)(B)^2 \tag{y}$$

Equation (x) involves a reverse reaction of the second order, while (y) is based upon a reverse reaction of the third order. When the experimental values are substituted, constant values are obtained for k_1 and k_2 (Equation y) while a drift of several hundred per cent. is observed in the values of k_1' and k_2' (Equation x).

KINETICS OF HYDROLYSIS AT 15°; PH 5.35

“ ”	(C)	$-d(C)dt$	(A)	(B)	k_2	k_2' (Eq. x)
0	0.01145	......	.....	.....	...	..
5	.01029	0.000221	0.00113	0.00229	131.2	0.30
10	.00907	.000195	.00227	.00464	135.0	0.63
15	.00837	.000167	.00291	.00599	131.8	..
20	.00760	.000137	.00358	.00743	130.7	..
25	.00695	.000119	.00412	.00862	142.7	1.2
30	,00645	.000088	.00457	.00957	137.5	..
35	.00605	.000063	.00490	.01030	137.0	1.5

$k_1 = K_{1a} \cdot k_2$ in (9), also the values of A and B in terms of αC_0 and solving for k_2, the velocity constant for the reverse reaction

$$k_2 = \frac{\dfrac{d(\alpha C_0)}{dt}}{C_{H^+} \cdot K_{1a}(C_0 - \alpha C_0) - \left[\dfrac{-(\alpha C_0 + 0.1) + \sqrt{(\alpha C_0 + 0.1)^2 + 0.4\alpha C_0}}{2}\right]} \times \frac{1}{\left[\dfrac{\alpha C_0 - 0.1 + \sqrt{(\alpha C_0 + 0.1)^2 + 0.4\alpha C_0}}{2}\right]^2}$$

Tangents drawn at suitable points on the curves give $d(\alpha C_0)/dt$ with sufficient accuracy.

By this method is obtained a value of $k_2 = 75.0$ at 20° and 135.0 at 15°; $k_1 \cdot C_H$ becomes 0.0294 at 20° and 0.0221 at 15°. This corresponds to a temperature coefficient of 2.65 for a 10° rise for the hydrolysis. On the other hand, the reverse reaction has a lower constant at 20° than at 15°. A rise in temperature will therefore shift the whole equilibrium markedly to the right, favoring the hydrolysis.

Having at hand the values of the equilibrium constant at two temperatures, ΔH may be found from the expression

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT_2}. \quad \text{From the data, } \Delta H = 9100 \text{ cal.}$$

It is also interesting to calculate the standard free energy change ΔF° for the reactions involved. For Equation 1a the formation of one mole of hydrazine ion and two moles of acetone from one mole of dimethylketazine, one mole of H^+ and two of water

$$\Delta F^\circ_{288} = -RT \ln K_{1a} = -1323 \log 37.0$$
$$\Delta F^\circ_{288} = -2075 \text{ cal.}$$

For Equation 1, the formation of one mole of acetone hydrazone and one mole of acetone from one mole of ketazine, one mole of H^+ and one mole of water

$$\Delta F^\circ_{288} = -RT \ln K_1 = -1323 \log 370$$
$$\Delta F^\circ_{288} = -3400 \text{ cal.}$$

These values are small, as would be expected with a reversible reaction, but taken as they stand would indicate that Reaction 1 is a more probable course for the reaction than 1a, and hydrolysis of dimethylketazine gives first acetone and acetone hydrazone, followed by hydrolysis of the hydrazone to give hydrazine ion and more acetone.

The author wishes to express his gratitude to the John Simon Guggenheim Memorial Foundation and the Regents of the Oregon State College for providing the opportunity for this study. He is especially indebted to Professor Bronsted for the hospitality of his laboratory and for suggestions in the prosecution of the work.

Summary

1. The hydrolysis of dimethylketazine has been studied at 15 and at 20° by a kinetic method.

2. The reaction is reversible and an equilibrium is reached involving H^+, dimethylketazine, acetone hydrazone, acetone and hydrazine.

3. Equilibrium constants have been evaluated under several conditions.

4. The kinetics of the reaction have been studied at the two temperatures and velocity constants for the forward and reverse reactions obtained.

5. Some of the free energy values have been calculated.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE RICE INSTITUTE]

THE EFFECT OF STRUCTURE OF ORGANIC HALIDES ON THEIR RATE OF REACTION WITH INORGANIC HALIDES.

III. THE EFFECT OF THE PHENYLTHIO, ALPHA-NAPHTHOXYL AND BETA-NAPHTHOXYL GROUPS

BY W. R. KIRNER AND G. HOLMES RICHTER

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Previous papers published from this Laboratory on the effect of structure of organic chlorides on their rate of reaction with potassium iodide in absolute acetone solution have included the effect of the phenoxyl and methylthio groups,[1] and it seemed of interest to determine how these rates would be affected by substituting an α- and β-naphthoxyl group for a phenoxyl, and a phenylthio group for a methylthio group. The data also give a comparison of the relative effect of an oxygen and sulfur atom in compounds of the structure $C_6H_5O(CH_2)_nCl$ and $C_6H_5S(CH_2)_nCl$. These comparisons are summarized in Table I.

A study of this table brings out the following relationships of structure to reactivity. 1. A chlorine atom in the β-position to a given group has a reactivity which is in every case less than the reactivity of the chlorine atom when in the γ-position to the same group. The ratio of these reactivities at 50° varies between 1:1.53 for the phenyl group, which is the smallest ratio, to 1:6.14 for the α-naphthyl group, which is the greatest.

2. The temperature coefficient ***A*** is in every case higher in the compounds with two carbon atoms between the chlorine and the activating group than in the corresponding compounds with three carbon atoms. The values for A in the first case average approximately 4600 and approximately 4150 in the second case.

3. A phenylthio group in the β- or γ-position to a chlorine atom causes the reactivity of that chlorine atom to be about twice as great as when a

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[1] Kirner, THIS JOURNAL, 48, 2745 (1926); *ibid.,* **50,** 2446 (1928).

TABLE I

COMPARATIVE DATA

Compound	K_{50}	K_{60}	A	Rel. reactivity at 50°, n-butyl chloride as unity
n-C_4H_9Cl[a]	0.0415	0.1189	4920	1.00
$CH_3SCH_2CH_2Cl$[b]	.0629	.1666	4540	1.52
$C_6H_5SCH_2CH_2Cl$	.0234	.0639	4706	0.56
$C_6H_5OCH_2CH_2Cl$[c]	.0124	.034	4710	0.30
$C_6H_5CH_2CH_2Cl$[a]	.0466	.108	3920	1.12
α-$C_{10}H_7OCH_2CH_2Cl$	.0136	.0398	5015	0.33
β-$C_{10}H_7OCH_2CH_2Cl$	.0137	.0384	4795	0.33
$CH_3SCH_2CH_2CH_2Cl$[b]	.1044	.2373	3830	2.52
$C_6H_5SCH_2CH_2CH_2Cl$	.114	.280	4198	2.74
$C_6H_5OCH_2CH_2CH_2Cl$[c]	.0694	.186	4600	1.67
$C_6H_5CH_2CH_2CH_2Cl$[a]	.0713	.160	3770	1.72
α-$C_{10}H_7OCH_2CH_2CH_2Cl$	.0835	.205	4200	2.01
β-$C_{10}H_7OCH_2CH_2CH_2Cl$	,0839	.212	4333	2.02

[a] Conant and Kirner, THIS JOURNAL, 46,235 (1924). [b] From the second paper of this series. [c] From the first paper of this series.

phenoxyl group is in the same position. This gives a direct comparison of the effect of the replacement of a sulfur atom by an oxygen atom.

4. The introduction of an oxygen or sulfur atom between the phenyl group and the @-carbonatom (with reference to the chlorine atom) decreases the reactivity of the chlorine atom; but the reactivity of the chlorine is increased if the oxygen or sulfur is introduced between the phenyl group and the γ-carbon atom.

5. 'She phenylthio group in the β-position to a chlorine atom produces a lower degree of reactivity than a methylthio group, but a greater reactivity when in the y-position. This is probably what the various theories of alternate polarity would predict on the basis of the greater negativity of the phenyl group compared to the methyl group.

6. An α- or β-naphthoxyl group in the β- or y-position to a chlorine atom has essentially the same effect as a phenoxyl group in the same position, possibly causing a very slightly greater reactivity. There is no detectable difference in the reactivity caused by an α- or β-naphthoxyl group.

The above conclusions are verified in the data collected in Table II, which compares the reactivities of the compounds RCH_2CH_2Cl and $RCH_2CH_2CH_2Cl$ with ethyl and n-propyl chloride, respectively. This table shows the effect of replacing a @-hydrogenin ethyl chloride and a y-hydrogen in n-propyl chloride by an R group. The additional relationship is brought out from this table that the introduction into the β-position with respect to the chlorine atom, of any of the groups considered, decreases the reactivity of the chlorine atom from $^{1}/_{2}$ to $^{1}/_{8}$ (depending on the particular R group) of its reactivity in the unsubstituted ethyl chloride. If the R group is introduced into the y-position with respect to the chlorine, the reactivity of the chlorine is increased from 1.5 to nearly **3** times its original reactivity in n-propyl chloride. From this viewpoint there appears to be a distinct alternation in reactivity; the substituting group, when in the β-position, depresses the reactivity below that of the unsubstituted chloride but exalts the reactivity above that of the unsubstituted chloride when in the y-position. However, the group which produces the greatest decrease in reactivity in the β-position does not necessarily produce the greatest exaltation when in the y-position.

TABLE II

CONFIRMATORY DATA

Compound	$\frac{RCH_2CH_2Cl}{CH_3CH_2Cl}$ 50°	60°	Compound	$\frac{RCH_2CH_2CH_2Cl}{CH_3CH_2CH_2Cl}$ 50°	60°
$C_2H_5Cl^a$	1.0	1.0	n-$C_3H_7Cl^a$	1.0	1.0
$CH_3SCH_2CH_2Cl^b$	0.62	0.85	$CH_3SCH_2CH_2CH_2Cl^b$	2.41	2.28
$C_6H_5SCH_2CH_2Cl$	.23	.33	$C_6H_5SCH_2CH_2CH_2Cl$	2.63	2.69
$C_6H_5OCH_2CH_2Cl^c$	.12	.17	$C_6H_5OCH_2CH_2CH_2Cl^c$	1.60	1.79
$C_6H_5CH_2CH_2Cl^d$	.46	.55	$C_6H_5CH_2CH_2CH_2Cl^d$	1.65	1.54
α-$C_{10}H_7OCH_2CH_2Cl$	.14	.20	α-$C_{10}H_7OCH_2CH_2CH_2Cl$	1.93	1.97
β-$C_{10}H_7OCH_2CH_2Cl$	.14	.20	β-$C_{10}H_7OCH_2CH_2CH_2Cl$	1.93	2.04

[a] Conant and Hussey, THIS JOURNAL, 47,477 (1925). [b] From the second paper of this series. [c] From the first paper of this series. [d] Conant and Kirner, *ibid.*, 46, 235 (1924).

While this work was in progress a paper appeared by Bennett and Berry[2] in which they also made the β-chloro-ethyl and y-chloropropyl phenyl sulfides and studied the rate of hydrolysis and also the rate of reaction with potassium iodide, using the method developed by Conant and Kirner. In the synthesis of these compounds they did not isolate the ω-hydroxyalkyl phenyl sulfides and they claim "an attempt to distil phenyl-β-hydroxyethyl sulfide under diminished pressure gave an unsaturated compound, probably due to the splitting out of water from the side chain, giving rise to phenyl vinyl sulfide." No mention is made of a similar attempt at the isolation of the y-hydroxy compound.

We were unable to confirm the statements of Bennett and Berry regarding the instability of the β-hydroxyethyl phenyl sulfide. We isolated this compound as well as the y-hydroxypropyl phenyl sulfide by vacuum fractional distillation at 2 mm. and used the pure hydroxy compounds for the preparation of the chlorides.

In calculating the molecular refraction, the value used for sulfur was n_D 7.97 (the atomic refraction of sulfur in organic sulfides), as given by Price and Twiss.[3] The exaltation in the molecular .refraction of com-

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[2] Bennett and Berry, J. *Chem. Soc.*, 130,1676 (1927).

[3] Price and Twiss, *ibid.*, 101, 1264 (1912).

pounds which have an unsaturated atom (in this case sulfur) conjugated with a double bond (in this case with a double bond in the phenyl group) as observed by Clarke and Smiles[4] was also found to occur in these phenylthio ethers, the exaltation averaging 0.52 unit. A similar exaltation occurred with the naphthoxyl ethers, in which oxygen is the unsaturated atom, the exaltation averaging 2.512 units.

Bennett and Berry also state that "Andrews' method for estimation of iodide in presence of chloride was found to be unsatisfactory in the present investigation owing to reaction between the iodic acid and the organic sulfide in the chloroform used for indicator. Even after removal of the organic compound the end-point with chloroform as indicator was not well defined." They therefore used the method of Lang,[5] which, as modified, appears to be considerably more tedious and requires both extraction with chloroform and steam distillation of each sample before titration.

In our work on these sulfur compounds we used Andrews' method of titration with the chloroform extraction recommended in previous papers. No difficulty was experienced with ill-defined end-points. The maximum deviation of the velocity constants obtained by us on the β-phenylthio compound was about 11% at both 50 and 60°, whereas Bennett and Berry had a deviation of 16%. Their deviation on the y-compound was but 6%, whereas ours was considerably higher and there was a marked drift in the constants, particularly at 60°, which, however, is not necessarily due to errors involved in the titration. Table III indicates the excellent agreement in the absolute values of Bennett and Berry's velocity constants compared with ours despite the fact that two different methods of titration were used and by different operators. It seems to us that this agreement establishes the Andrews' method as yielding satisfactory results. Our results are calculated to 55° by the use of the temperature coefficient A.

TABLE III

COMPARATIVE DATA

	K_{55}	
	K. and R.	B. and B.
$C_6H_5SCH_2CH_2Cl$	0.0389	0.0395
$C_6H_5SCH_2CH_2CH_2Cl$	.1798	.1434

Vesicant Action of the Chloro Sulfides.—A good-sized drop of the β-compound was placed on the right forearm with a 4 mm. glass rod and a similar drop of the y-compound on the left forearm. The β-compound was either absorbed or evaporated more rapidly than the y-compound. After about four hours a reddened area, the size of a hen's egg, developed on the right forearm due to the action of the β-compound. This spot

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[4] Clarke and Smiles, J. *Chem. Soc.*, 95, 997 (1909).

[5] Lang, Z. *anorg. Chem.*, 122, 332 (1922).

became quite sore to the touch and after five days there was an incipient blistering of the skin. A brownish stain persisted for several months. The y-compound produced no effect whatsoever.

The β-chloro-ethyl phenyl sulfide is thus seen to be considerably less vesicant than the β-chloro-ethyl methyl sulfide. The conclusions reached in the second paper of this series[6] were completely verified.

Experimental

I. The Phenylthio Series

A. Preparation of the **ω-Phenylthio-alkyl** Chlorides.—The first member of this series, phenylthiomethyl chloride, is missing and no attempt was made to synthesize it because of previous unsuccessful attempts to prepare both its oxygen analog and methylthiomethyl chloride.[7]

1. Preparation of **β-Hydroxyethyl** and y-Hydroxypropyl Phenyl Sulfides.—The most recent attempt recorded in the literature to synthesize these substances is that of Bennett and Berry,[2] who treated sodium thiophenoxide with ethylene and trimethylene chlorohydrin, respectively. They did not succeed in isolating these substances in a pure state and therefore did not characterize them; they merely used the crude product from the reaction mixture for another reaction. Steinkopf, Herold and Stohr[8] made the (3-hydroxy compound in a similar manner but made no attempt to isolate it.

The method used in this work was analogous to that suggested by Powell for the preparation of the oxygen analogs.[9] Fifty grams (0.454 mole) of thiophenol was dissolved in 180 cc. of 10% sodium hydroxide solution (0.045 mole), and then treated with slightly more than the theoretical amount of the desired chlorohydrin. The reaction took place rapidly and the mixture was refluxed for half an hour to insure its completion. The oily layer was separated, the aqueous layer extracted twice with ether and the combined oil-ether layer washed with water and dried over anhydrous sodium sulfate. The ether was distilled off, leaving a practically quantitative yield of nearly pure product which was carefully fractionated several times under reduced pressure from a Claisen fractionating flask. Phenyl (3-hydroxyethylsulfide is a water-white liquid with a rather sweet, not unpleasant odor.

Anal. Subs., 0.2160: $BaSO_4$, 0.3241. Calcd. for $C_8H_{10}OS$: S, 20.79. Found: S, 20.61.

There was no difficulty whatsoever experienced during the fractional vacuum distillation and there was no evidence of unsaturated compound formation as reported by Bennett and Berry. They did not state at what pressure their distillation was carried out, but at 1–2 mm. the above hydroxy compound distils smoothly and without decomposition and yields a pure product, as indicated by the analysis.

Phenyl **γ-hydroxypropyl** sulfide is a water-white liquid.

Anal. Subs., 0.1808: $BaSO_4$, 0.2490. Calcd. for $C_9H_{12}OS$: S, 19.06. Found: S, 18.91.

2. Preparation of **β-Chloro-ethyl** and y-Chloropropyl Phenyl Sulfides.—The β-chloro-ethyl compound was first prepared by Steinkopf and co-workers8 by passing hy-

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[6] Kirner, THIS JOURNAL, 50, 2449 (1928).

[7] Kirner, *ibid.*, 48, 2747 (1926); 50,2451 (1928).

[8] Steinkopf, Herold and Stohr, Ber., 53, 1012 (1920).

[9] Powell, THIS JOURNAL, 45,2709 (1923); Kirner, *ibid.*, 48, 2748 (1926).

drogen chloride into the crude hydroxy compound. They give the boiling point as 144.5" at 26 mm. and 245° at atmospheric pressure; yield, 76%. Lecher and Stöcklin[10] also obtained it in good yield by the addition of phenyl sulfur chloride to ethylene. They give the boiling point as 122° at 13 mm. and mention the vesicant action of the compound. Bennett and Berry made both the β-chloro-ethyl and y-chloropropyl compounds by the application of Darzens' reaction to the corresponding hydroxy compounds. They give the boiling point of the β-chloro-ethyl compound as 117° at 12 mm. and the boiling point of the γ-chloropropyl compound as 137° at 13 mm.; they state that the ethyl compound has a very slight vesicant action and that the propyl compound is not appreciably vesicant.

In this work the alcohols previously described were converted into the chlorides by Darzens' method,'' using thionyl chloride and pyridine. Twenty grams of the alcohol was treated with the theoretical amount of pyridine and about a 25% excess of thionyl chloride was added dropwise. The characteristic precipitate appeared after about half of the thionyl chloride had been added but redissolved on further addition, forming two layers. The sulfur dioxide was removed by heating on a steam-bath. The yield of crude product was quantitative and the yield after several vacuum fractionations was 80–85%.

β-Chloro-ethyl phenyl sulfide is a colorless liquid.

Anal. Subs., 0.1460, 0.2172: $BaSO_4$, 0.1983, 0.2925. Calcd. for C_8H_9SCl: S, 18.58. Found: S, 18.65, 18.50.

γ-Chloropropyl Phenyl Sulfide.—Anal. Subs., 0.2014, 0.2066: $BaSO_4$, 0.2525, 0.2565. Calcd. for $C_9H_{11}SCl$: S, 17.18. Found: S, 17.20, 17.06.

The physical constants of the phenyl sulfides are given in Table IV.

TABLE IV

PHYSICAL CONSTANTS OF PHENYL SULFIDES

Phenyl sulfide	B. p., °C.	d^{20}_{20}	d^{20}_4	n^{20}_D	M_D Calcd.	M_D Obs.	Exaltation
β-Hydroxyethyl	115–116 (2 mm.)	1.1451	1.1431	1.5917	45.038	45.611	0.573
y-Hydroxypropyl	134–135 (2 mm.)	1.1197	1.1178	1.5813	49.656	50.158	.502
β-Chloro-ethyl	100–101 (4 mm.)	1.1829	1.1808	1.5838	48.380	48.904	.524
γ-Chloropropyl	116–117 (4 mm.)	1.1556	1.1536	1.5752	52.998	53.471	.473

B. Reaction Velocity Measurements

TABLE V

REACTION BETWEEN β-CHLORO-ETHYL PHENYL SULFIDE AND POTASSIUM IODIDE (WITH EXTRACTION)

At 50° Time, hours	At 50° Reacted, %	At 50° K	At 60° Time, hours	At 60° Reacted, %	At 60° K
12.70	11.67	0.0215	6.0	16.33	0.0656
24.0	22.46	.0236	12.5	30.43	.0652
49.3	40.17	.0237	12.85	31.49	.0661
76.0	54.26	.0238	18.50	42.18	.0674
100.33	64.34	.0242	25.50	49.59	.0618
	Mean	.0234	35.75	60.17	.0602
			50.10	72.29	.0611
				Mean	.0639

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[10] Lecher and Stocklin, *Ber.*, 58, 414 (1925).

[11] Darzens, *Compt.* rend., 152, 1314 (1911).

Table V (Concluded)

Reaction between α-Chloropropyl Phenyl Sulfide and Potassium IodidE (with Extraction)

At 50°			At 60°		
Time, hours	Reacted, %	K	Time, hours	Reacted, %	K
2.50	13.17	0.124	1.0	15.50	0.372
5.25	25.52	.125	2.0	24.56	.314
11.0	42.55	.115	4.0	40.77	.298
15.0	52.15	.114	7.5	57.94	.269
20.0	59.58	.106	11.5	67.07	.228
26.5	67.30	.100	17.10	75.68	.198
	Mean	.114		Mean	.280

II. The α-Naphthoxyl Series

A. Preparation of the w-Chloro-alkyl a-Naphthyl Ethers.—The first members of both the *a*- and β-series are unknown and their synthesis was not attempted.

1. Preparation of **β-Hydroxyethyl** and y-Hydroxypropyl **α-Naphthyl** Ethers.—The @-hydroxyethylether was first prepared by Boyd and Marle[12] by treatment of ethylene oxide with sodium a-naphthoxide. They give the melting point as 42". In this work these substances were made analogously to the method used for the preparation of the phenylthio ethers described above. The reactions go rapidly, the emulsion appearing in about ten minutes and the reaction appears to be completed a few minutes later. The mixture is worked up in the usual way; it was found necessary to carry out several extractions of the oily ether layer with 5% sodium hydroxide solution to remove excess or-naphthol.

β-Hydroxyethyl α-naphthyl ether boiled at 167° at 2 mm It had a light yellow color. Numerous attempts were made to crystallize it from various solvents, simple and mixed, but they all failed. On long standing in an ice box the oil started to crystallize but the best melting point obtainable was 22–24°. It is possible that some decomposition occurred during distillation which caused the melting point to be so much lower than that reported by Boyd and Marle.

y-Hydroxypropyl **α-naphthyl** ether is a new compound. It was crystallized from petroleum ether, giving a pure white mass of needle-shaped rosets; m. p. 65.5–66.5°; yield (crude), 79%.

Anal. Subs., 0.2082: CO_2, 0.5894; H_2O, 0.1362. Calcd. for $C_{13}H_{14}O_2$: C, 77.19; H, 6.98. Found: C, 77.27; H, 7.32.

2. Preparation of **β-Chloro-ethyl and γ-Chloropropyl** a-Naphthyl Ethers.—Clemo and Perkin[13] first made the β-chloro-ethyl compound by the direct introduction of the chloro-ethyl group into a-naphthol, using β-chloro-ethyl *p*-toluenesulfonate. They give the melting point as 28° and the boiling point as 202" at 16 mm. We obtained this compound by carrying out a Darzens reaction on the corresponding alcohol, using pyridine and thionyl chloride. The sulfur dioxide was removed by heating on a water-bath for two hours; yield of crude product, 85%. This was carefully fractionated three times in a vacuum, giving a 61% yield of highly purified material. β-Chloro-ethyl or-naphthyl ether is a rather viscous, yellow oil which did not crystallize.

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[12] Boyd and Marle, J. Chem. *Soc.*, 105,2135 (1914).

[13] Clemo and Perkin, *ibid.*, 121,646 (1922).

Anal. Subs., 0.2718: AgCl, 0.1891. Calcd. for $C_{12}H_{11}OCl$: Cl, 17.16. Found: Cl, 17.21.

γ-Chloropropyl α-naphthyl ether is a new compound. It was prepared by the method just described; yield of twice distilled product, 54%. The compound is a light yellow, viscous liquid which did not crystallize.

Anal. Subs., 0.3034: AgCl, 0.1996. Calcd. for $C_{13}H_{13}OCl$: Cl, 16.07. Found: Cl, 16.27.

The physical constants of the a-naphthyl ethers are given in Table VI.

TABLE VI

PHYSICAL CONSTANTS OF α-NAPHTHYL ETHERS

a-Naphthyl ether	B. p., ° C.	d^{20}_{20}	d^{20}_{4}	n^{20}_{D}	M_D Calcd.	M_D Found	Exaltation
β-Hydroxyethyl	167° (2 mm.), m. p. 22–24"						
y-Hydroxypropyl	65.5–66.6 (m. p.)						
β-Chloro-ethyl	145–147(1.5 mm.)	1.1993	1.1972	1.6139	57.391	60.122	2.731
γ-Chloropropyl	167–168(1 mm.)	1.1686	1.1665	1.6025	62.009	64.903	2.894

B. Reaction Velocity Measurements

TABLE VII

REACTION BETWEEN β-CHLORO-ETHYL α-NAPHTHYL ETHER AND POTASSIUM IODIDE

At 50°			At 60°		
Time, hours	Reacted, %	K	Time, hours	Reacted, %	*K*
25.1	14.00	0.0132	13.0	18.84	0.0356
25.1	13.33	.0126	24.33	35.61	.0409
50.05	26.92	.0140	38.55	49.76	.0411
75.0	37.44	.0142	50.0	58.90	.0415
100.5	46.05	.0141	66.7	67.60	.0400
	Mean	.0136		Mean	.0398

REACTION BETWEEN α-CHLOROPROPYL α-NAPHTHYL ETHER AND POTASSIUM IODIDE

At 50°			At 60°		
Time, hours	Reacted, %	*K*	Time, hours	Reacted. %	*K*
3.0	11.50	0.0895	1.0	8.17	0.187
7.25	23.88	.0838	2.0	17.44	.212
12.50	37.48	.0851	4.0	31.45	.212
15.75	44.24	.0847	6.0	43.76	.219
20.50	51.55	.0815	8.0	52.31	.214
30.90	63.39	.0764	11.25	61.01	.196
	Mean	.0835	15.10	71.36	.197
				Mean	.205

III. The β-Naphthoxyl Series

A. Preparation of the ω-Chloro-alkyl β-Naphthyl Ethers

1. Preparation of **β-Hydroxyethyl** and **γ-Hydroxypropyl β-Naphthyl** Ethers.— This **β-hydroxyethyl** ether was also made by Boyd and Marle. They give the melting point as 76°. Rindfusz, Ginnings and **Harnack**[14] made it by treatment of sodium β-

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[14] Rindfusz, Ginnings and Harnack, THIS JOURNAL, 42, 164 (1920).

naphthoxide with ethylene chlorohydrin; m. p. 76–77°. We obtained it using precisely the same method that was used for the a-isomer. Crystallization from a mixture of one part of benzene and two parts of petroleum ether gave a product melting at 75–76°; yield of pure product, 57%.

The γ-hydroxypropyl ether was also prepared by Rindfusz and co-workers with a 25% yield; m. p. 99–99.5°. We found the preparation of this compound to go more slowly than the ethyl ether. Crystallization from a mixture of benzene and petroleum ether gave the pure product melting at 98.7–99.4°; yield, 38%

2. Preparation of β-Chloro-ethyl and γ-Chloropropyl β-Naphthyl Ethers.—Clemo and Perkin also made this chloro-ethyl ether. A quantitative yield of crude product was obtained. The pure crystallized compound melted at 83°. We obtained the compound by the Darzens reaction on the alcohol, the crude product also being obtained in quantitative yield. Repeated crystallization from 95% alcohol gave a pure product melting at 80–81°.

Anal. Subs., 0.3217: AgCl, 0.2199. Calcd. for $C_{12}H_{11}OCl$: Cl, 17.16. Found: Cl, 16.91.

γ-Chloropropyl β-naphthyl ether is a new compound and was made by the procedure already described; the yield of crude product was 96%. Crystallization from absolute alcohol gave pure white crystals melting at 47–47.5°.

Anal. Subs., 0.3020: AgCl, 0.1966. Calcd. for $C_{13}H_{13}OCl$: Cl, 16.07. Found: Cl, 16.10.

B. Reaction Velocity Measurements

Table VIII

Reaction between β-Chloro-ethyl β-Naphthyl Ether and Potassium Iodide

At 50°			At 60°		
Time, hours	Reacted, %	K	Time, hours	Reacted, %	K
16.0	9.50	0.0137	13.0	20.77	0.0398
26.0	15.43	.0142	24.5	34.72	.0393
50.1	27.30	.0142	35.5	45.10	.0386
75.0	36.20	.0136	49.2	55.49	.0382
100.5	43.62	.0130	67.6	64.39	.0359
	Mean	.0137		Mean	.0384

Reaction between γ-Chloropropyl β-Naphthyl Ether and Potassium Iodide

At 50°			At 60°		
Time, hours	Reacted, %	K	Time, hours	Reacted. %	K
5.0	17.92	0.0874	2.0	18.57	0.228
10.1	32.52	.0876	4.0	32.87	.224
15.6	43.69	.0840	6.75	48.07	.223
25.25	56.48	.0766	8.0	51.54	.209
	Mean	.0839	10.4	59.18	.201
			15.0	69.51	.188
				Mean	.212

Summary

1. The effect of the phenylthio and α- and β-naphthoxyl groups upon the reactivity of a chlorine atom in the β- and y-positions has been determined by studying the velocity with which the chlorine is replaced

by iodine using potassium iodide in absolute acetone solution. A comparison was made of the effect of these groups with the methylthio, phenoxyl and phenyl groups when similarly situated.

2. β-Chloro-ethyl phenyl sulfide was found to have only a weak vesicant action and the y-chloropropyl phenyl sulfide was completely non-vesicant.

3. The following substances were isolated and characterized for the first time: β-hydroxyethyl phenyl sulfide, y-hydroxypropyl phenyl sulfide, y-hydroxypropyl a-naphthyl ether, y-chloropropyl a-naphthyl ether, y-chloropropyl β-naphthyl ether.

HOUSTON, TEXAS

[A COMMUNICATION FROM THE LABORATORY OR ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

COMPETITIVE HYDROGENATIONS

BY HOMER ADKINS, F. F. DIWOKY AND A. E. BRODGRICK

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The importance of precise information on the relation of the structure of a compound to its reactivity as manifested in the ease of reduction led Vavon and Husson[1] to devise a unique method for the experimental study of the rate of reduction of certain derivatives of cinnamic acid. Their method consisted in adding one mole of hydrogen to a mixture of one mole of d-a-pinene and one mole of the compound under consideration, and then calculating the distribution of the hydrogen between the two compounds from the change in optical activity of the mixture. They assumed that the distribution of the hydrogen between the pinene and the unsaturated compounds was a measure of the ease of reduction of the unsaturated compounds. If, for example, cinnamic acid took up 57% of the hydrogen (pinene 43%) and a-methylcinnamic acid took up 26% (pinene 74%), they concluded that cinnamic acid was reduced much more easily than the substituted acid. This method of comparison has two very considerable advantages over the usual one of noting the rate of absorption of hydrogen by a single compound. The latter method for an accurate comparison demands that the comparisons be made over catalysts of identical activity. This is a condition which it is difficult if not impossible to meet if an extended list of compounds is to be compared. This method also presupposes that there is no impurity in any of the compounds which would lower the activity of the catalyst. An attempt was made to repeat and extend their work because of our interest in simultaneous reactions and because previous work in this Laboratory made it seem probable that the ratio of the distribution would be a func-

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[1] Vavon and Husson, *Compt.* rend., 176, 989 (1923).

tion of the particular catalyst and the solvent used as well as of the structure of the organic compounds reduced.

Four hundredths of a mole of d-a-pinene and 0.04 of a mole of cinnamic acid or other unsaturated compound were mixed in a solvent and the volume made up to 100 cc. A quantity of Adams and Voorhees' platinum oxide was added and followed by 0.04 mole of hydrogen under a pressure of 0.2 of an atmosphere. The bottle containing the reaction mixture was agitated. A polarimetric reading of the mixture was taken before and after the addition of hydrogen. A second solution containing only d-a-pinene was fully reduced and the rotation noted. The distribution of the hydrogen between the two compounds may be calculated from the readings on the hydrogenated pinene, the unreduced mixture and the mixture after absorption of one mole of hydrogen. Whenever a new catalyst was prepared, its activity was standardized by a trial run. Allowance was made for the volume of hydrogen absorbed by the platinum oxide on being reduced to platinum black. All of the results given in this paper were checked at least once and most of them several times, using different preparations of catalyst and solvent.

There is no very marked difference in the rate of reduction of a mixture of pinene and cinnamic acid irrespective of whether methyl *(33* m.) or ethyl alcohol *(37* m.) or acetic acid (40 m.) is used. The rate is much lower in ethyl acetate (70 m.) and the higher alcohols propyl (65 m.) and butyl (85 m.). Ferrous sulfate has no effect upon the rate but 0.001 mole of manganese (55 m.) and especially zinc (180 m.) and nickel acetates (180 m.) very greatly reduce the rate of hydrogenation. There was very little difference in the rate of reduction of mixtures in acetic acid of pinene and cinnamic acid (40 m.), a-methylcinnamic acid (35 m.), methyl β-methylcinnamate (33 m.) and ethyl β-methylcinnamate (33 m.).

TABLE I

REDUCTION OF PURE COMPOUNDS AND MIXTURES

Time for reduction in minutes Cinnamic acid	Pinene	Mixture	H_2 to pinene, %	Solvent	Catalyst
31	5	25	35	CH_3CO_2H	0.095 g. Pt oxide
83	124	60	18	$CH_3CO_2C_2H_5$	.095 g. Pt oxide
		41	15	$CH_3CH(OC_2H_5)_2$	.285 g. Pt oxide
		19	19	$(CH_2OCH_3)_2$	.285 g. Pt oxide
59	92	59	14	CH_3COCH_3	.095 g. Pt oxide
..	..	200	20	None	10 g. Ni and kieselguhr
"Octene," 6	5	6	24	CH_3CO_2H	0.095 g. Pt oxide
		200	53	None	10 g. Ni and kieselguhr
Cyclohexene, 8	5	7	15	CH_3CO_2H	0.095 g. Pt oxide
Allyl alcohol, 34	5	6	8	CH_3CO_2H	.095 g. Pt oxide
α-Methylcinnamic acid	..	..	93	CH_3CO_2H	.10 g. Pt oxide
Methyl β-methylcinnamate	..		87	CH_3CO_2H	.30 g. Pt oxide
Ethyl β-methylcinnamate	..		91	CH_3CO_2H	.30 g. Pt oxide

The data referred to in the last paragraph were obtained at an earlier time and with samples of catalysts which differed somewhat in activity from those referred to in Table I. In Col. 1 of this table is given the time in minutes for the addition of 0.04 mole of hydrogen to 0.04 mole of cinnamic acid or other unsaturated compound. In Col. 2 is given the time required for the similar reduction of pinene and in Col. **3** is given the time required for the addition of 0.04 mole of hydrogen to a mixture of 0.04 mole of pinene and 0.04 mole of the other unsaturated compound under consideration. The percentage of the hydrogen taken up by the pinene is given in Col. 4.

The nature of the solvent and the structure of the cinnamic acid derivatives play a very large role in determining the ratio of distribution of the hydrogen between the compounds of the mixture, as has been pointed out by Vavon and his associates. In an acetic acid solution of cinnamic acid and pinene, 65% of the hydrogen goes to the acid, while in ethyl acetate, acetal or the dimethyl ether of ethylene glycol the acid receives from 81 to 85% of the hydrogen. In an acetic acid solution a-methylcinnamic acid gets only 7% of the hydrogen, while the esters of β-methylcinnamic acid get only 9 to 13% of the hydrogen.

In acetic acid solution Vavon and Husson found that 57% of the hydrogen went to the cinnamic acid, 26% to the a-methylcinnamic acid, 45% to the methyl β-methylcinnamate and 31% to the ethyl β-methylcinnamate. Our results are in only fair agreement with those of Vavon and Husson for cinnamic acid and are markedly different for the derivatives of the acid. It is not believed that this is a reflection on the work of either set of investigators, but shows, rather, that the nature of the pinene used affects the distribution of hydrogen. It should be noted that our platinum catalysts were not prepared by the same method as that used by Vavon and his associates.

The salts which have so great an influence on the rate by hydrogenation had no effect upon the distribution of hydrogen between the two unsaturated compounds present in the mixture. The activity of the catalyst is entirely without effect upon ratio of the distribution of the hydrogen.

The most striking results noted in this study have to do with the rates of reduction of pure compounds as compared to the reduction of mixtures. Pinene is much more rapidly reduced in acetic acid solution than is cinnamic acid, yet in a mixture the acid is reduced more rapidly than is pinene. Pinene and octene are reduced at very similar rates, yet in a mixture the octene gets about 75% of the hydrogen. It requires almost seven times as long to reduce a mole of allyl alcohol as it does one of pinene, yet in a mixture allyl alcohol gets 92% of the hydrogen at a rate very similar to that for pinene. These results show that there may be no relationship between the relative rates of reduction of pure compounds and their rate of reduction in mixtures.

An attempt was made to find a set of conditions under which the distribution of hydrogen between two compounds could be studied over both a platinum and a nickel catalyst. This was unsuccessful, since nickel is not active toward the compounds under consideration at room temperature, nor in the presence of ethyl acetate or acetic acid. Platinum is apparently not active at the higher temperatures at which nickel functions as a catalyst. Mixtures of 0.25 mole of cinnamic acid and 0.25 mole of pinene and of octene and pinene were hydrogenated at 135° in a glass container at a pressure of from one to two atmospheres using 10 g. of Reid and Rather's[2] nickel catalyst reduced for two hours at 450°. The calculated distribution of hydrogen between the competing compounds is given in Table I.

Reduction of Furfural Acetone.—Since the solvent apparently plays so large a role in determining the relative rates of reduction of various pairs of unsaturated compounds, some experiments were carried out on a larger scale upon the reduction of furfural acetone, which contains four points of unsaturation in the molecule.

One-half mole of hydrogen was added to 0.5 mole of furfural acetone in 125 cc. of the solvent at from one to three atmospheres' pressure of hydrogen, using 0.2 g. of catalyst in alcohol and ethyl acetate and 0.5 g. of a less active catalyst in petroleum ether. The hydrogenation was complete in three to four hours. The larger amount of catalyst used in the petroleum ether was necessary in order to complete the reduction in the usual time as the hydrocarbon mixture apparently dissolved rubber from the stopper of the hydrogenation bottle and thus the catalyst became poisoned. Six of these reaction products were combined (total 540 g.) and fractionated six times at 3 mm. through a 50-cm. Vigreux column (see Table II). The second fraction boiled at 201–202° at atmospheric pressure and the third melted at 38–39'. The semicarbazones from the second fractions melted at 143°. These values show that the fractions were almost pure 4-α-furfurylbutanone-2 and furfural acetone, respectively. The lower fractions consisted very largely of the butanone and the third fraction was made up largely of furfural acetone.

TABLE II

HYDROGENATION OF FURFURAL ACETONE IN VARIOUS SOLVENTS

Solvent	% in various fractions				Total distillate. %
	50–77.5°	77.5–78 5° 4-α-Furfuryl butanone-2	78.5–95°	95–97° Furfural acetone	
C_2H_5OH	10.6	36.1	9.6	12.2	68.5
$CH_3COOC_2H_5$	4.4	25.7	8.5	35.1	73.7
C_nH_{2n+2}	8.6	48.6	14.1	16.0	87.3

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[2] Reid and Rather, THIS JOURNAL, 37,2116 (1915).

A comparison of ethanol, ethyl acetate and petroleum ether as solvents for the reduction of furfural acetone shows that much more furfural acetone was left after the addition of the hydrogen when ethyl acetate was used as a solvent. This means that this solvent facilitated the addition of more than one molecule of hydrogen to a molecule of the ketone, thus causing more complete hydrogenation and poorer yields of 4-a-furfurylbutanone-2. Ethyl alcohol facilitated resinification so that although the yield of the 4-a-furfurylbutanone-2 was higher than with ethyl acetate the recovery of furfural acetone was very low. Petroleum ether did not facilitate the complete hydrogenation noted with ethyl acetate, nor was resinification so high, so that excellent yields of the 4-a-furfurylbutanone-2 were obtained.

Reagents

d-α-**Pinene** was obtained through the kindness of Professor Floyd E. Rowland of the Oregon Agricultural College and the Western White Cedar Co., Marshfield, Oregon. It came from a source which yields a pinene having the highest specific rotation that has been reported in the literature.[3] Its constants were those given by Dr. Thurber, i. e., b. p. 156–156.5°, $[\alpha]_{D}^{20}$ +53.01. The authors were very fortunate to obtain this pure d-or-pinene as the pinene separated from ordinary American turpentine has only a small optical activity. Vavon and Husson presumably used pinene from French turpentine, which contains a much larger proportion of the dextro isomer than does ordinary American turpentine.

Platinum oxide was prepared as by Adams, Voorhees and Shriner.[4] The platinum black after use was converted to platinic chloride either by the method described in their papers, using hydrobromic acid or by dissolving in aqua regia. After several such recoveries the platinum was purified as by Wichers.[5]

Allyl alcohol was purified according to the method of "Organic Syntheses."[6] It absorbed the theoretical quantity of hydrogen and distilled at 95.5–96.5". The petroleum ether was an Eastman Kodak Company product purified by permanganate and boiling at 35–60°. Furfural acetone was prepared as indicated in "Organic Syntheses,"[7] and showed a melting point of 38". The octene used was that isomer known as di-*iso*-butylene and was prepared from tertiary butyl alcohol by Walter Arthur, using a method similar to that described by Edgar.[8] It boiled at 101° at 742 mm. and absorbed the theoretical amount of hydrogen. The cyclohexene was fractionated so that the sample used had a boiling-point range from 81.9 to 82.1". It absorbed 96% of the theoretical quantity of hydrogen.

The cinnamic acid was purified from a commercial product by repeated recrystallization from a mixture of 60% alcohol and 40% water. The melting point was 133°. The α-methylcinnamic acid (m. p. 74–76") was made by a standard laboratory method for cinnamic acid by substituting sodium propionate and propionic anhydride for the

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[3] Thurber, *Ind.* Eng. Ckem., **19,** 739 (1927).

[4] Voorhees and Adams, THIS JOURNAL, **44,** 1397 (1922); Adams and Shriner, ibid., 45, 2171 (1923).

[5] Wichers, ibid., **43,** 1268 (1921).

[6] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1921,** Vol. II, p. 15.

[7] "Organic Synthescs," John Wiley and Sons, Inc., New York, **1927,** Vol. VII, p. 42.

[8] Edgar, Ind. *Eag.* **Ckem., 19, 146** (1927).

corresponding acetates. The methyl (b. p. 152" (26 mm.)) and ethyl (b. p. 162–163° (26 mm.)) esters of β-methylcinnamic acid were made as described by Lindenbaum[9]

Summary and Conclusions

It appears that the factors determining the distribution of hydrogen by platinum between two competing reactants, like the factors determining the proportion of dehydration and dehydrogenation of an alcohol over zinc oxide, for example,[10] bear little relationship to those factors which determine the amount of material reacting in unit time. The addition of zinc and nickel acetates, for example, retarded the rate of reduction but did not modify the distribution of hydrogen. The use of acetic acid, ethyl acetate and various alcohols as solvents modified the rate of reaction of hydrogen and in addition determined in part the ratio of its distribution between the two reactants. It seems that the salts poison the catalyst for the reaction of the two unsaturated compounds to an equal extent,[11] presumably through adsorption in certain areas of the catalyst. It may be suspected that in addition to this the solvent plays a part in the rate of formation and the stability of an intermediate compound of platinum–hydrogen–reactant–solvent.

The relative ease of reduction of two substances in a mixture may not be certainly determined even qualitatively by determining the rates of reduction of the two substances separately.

In the reduction of furfural acetone there are three competing reactions: (1) simple hydrogenation of the alkene linkage in the open chain, (2) the addition of more than one molecule of hydrogen to a molecule of the ketone and *(3)* "resinification." The ratio of these reactions may be markedly changed by varying the solvent.

The esterification of cinnamic acid or the substitution of a methyl group for a hydrogen on the a- or @-carbonatom very greatly reduced the proportion of hydrogen going to the alkene linkage when the compounds in a mixture with d-a-pinene were treated with hydrogen. No considerable difference was observed between the adsorption of hydrogen by the methyl and ethyl esters of β-methylcinnamic acid.

MADISON, WISCONSIN

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[9] Lindenbaum, *Ber.*, 50, 1270 (1917).

[10] Adkins and Lazier, THIS JOURNAL, 48, 1671 (1926).

[11] Cf. Tuley and Adams, *ibid.*, 47, 3061 (1925).

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

THE REGULARITIES IN THE MELTING POINTS OF SOME CRYSTALLINE DERIVATIVES OF VARIOUS ALIPHATIC ALCOHOLS[1]

BY G. B. MALONE[2] AND E. EMMET REID

RECEIVED JUNE 3, 1929 PUBLISHED NOVEMBER 8, 1929

Introduction

The fact that certain regularities exist in the melting points of various homologous series of aliphatic organic compounds is well known. As early as 1877 Baeyer[3] pointed out a definite alternation in the melting points of the saturated dibasic acids. Tsakalotos[4] and Forcrand[5] investigated the hydrocarbons of the methane series, while Biach[6] and Timmermans[7] made rather exhaustive investigations of many different series, the latter concluding that the alternation in melting points between the odd and even members of homologous series is a general phenomenon and attempting an explanation on the basis of the symmetry and spatial structure of the molecule. Tammann,[8] Cuy,[9] Pauly[10] and Garner and his co-workers[11] have studied the same general phenomenon of the fatty acids somewhat at length. This brief summation is by no means exhaustive, but it illustrates the type of work done. Throughout very little is said of the melting points of the alcohols themselves. Such alternation as may be seen from an examination of the melting points is much smaller than that of the hydrocarbons and fatty acids for example, and it was thought consequently that the alternate high and low melting points might be much more pronounced in a series of derivatives of the alcohols from one to ten carbon atoms. Such regularities have been found in a series of ketones, homologs of acetophenone,[12] in which the alkyl varies from C_{10} to C_{17}. Accordingly, the 3,5-dinitrobenzoates of the normal

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[1] Presented at the Columbus Meeting of the American Chemical Society, May, 1929.

[2] From a section of the Ph. D. dissertation of G. B. Malone, 1929.

[3] Baeyer, *Ber.*, 10, 1286 (1877).

[4] Tsakalotos, *Compt. rend.*, 143, 1235 (1907).

[5] Forcrand, *ibid.*, 172, 31 (1921).

[6] Biach, *Z. physik. Chem.*, **50**, 43 (1905).

[7] Timmermans, (a) *Bull. soc. chim. Belg.*, 25, 300 (1912); (b) *ibid.*, 27, 334 (1914); (c) *ibid.*, 28, 392 (1919); (d) *ibid.*, 30, 62 (1921); (e) *ibid.*, 30, 89 (1921).

[8] Tammann, *Z. anorg. allgem. Chem.*, 109, 221 (1920).

[9] Cuy, *ibid.*, 115, 273 (1921).

[10] Pauly, *ibid.*, 119, 271 (1922).

[11] (a) Garner and Randall, *J. Chem. Soc.*, 125, 881 (1924); (b) Garner and Ryder, *ibid.*, 127, 720 (1925); (c) Garner, Madden and Rushbrooke, *ibid.*, 2491 (1926); (d) Garner and Rushbrooke, *ibid.*, 1351 (1927).

[12] Majima, Nagaoka and Yamada, *Ber.*, 55, 215 (1922).

alcohols from methyl to decyl were prepared because there have been more of these particular derivatives reported for these alcohols than any of the standard ones. Later this series was supplemented with an iso (homologs of *iso*butyl, *iso*-amyl, etc.) and a secondary (hydroxyl on carbon atom number two) series.

Discussion of Results

The accompanying figure shows the melting points of the three abovementioned series of esters plotted against number of carbon atoms. The iso series extends to octyl and the secondary series to nonyl. In the normal series the alternating effect may be seen all the way through (with the esters of an even number of carbon atoms in the aliphatic portion high and those of odd carbon atoms low). With the lower members the effect is not so pronounced, in view of the low percentage of the molecular weight due to the alkyl part of the ester. The *iso* series shows the same type of curve except for a slightly greater tendency toward convergence and that the general swing of the curve has not reached a minimum

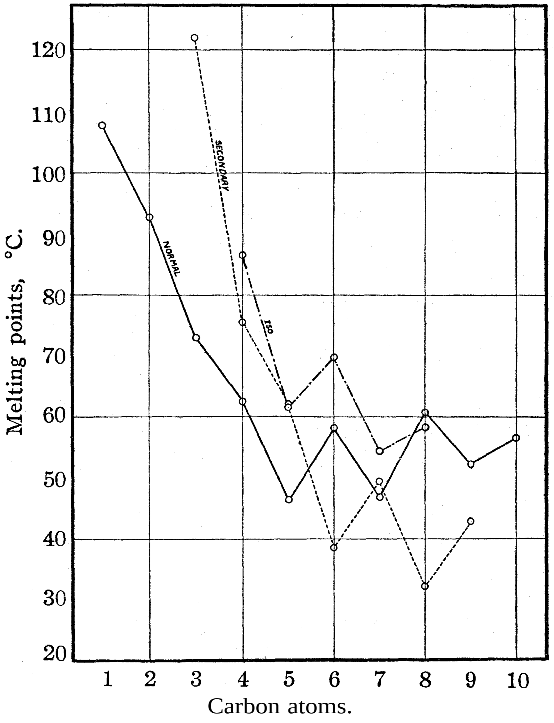
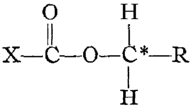


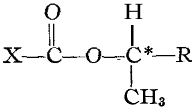
Fig. 1.—Melting points of alkyl esters of 3,5-dinitrobenzoic acid.

and started back up again, which would probably be the case could the curve be extended.

The secondary series offers an interesting variation. Here the esters of odd-numbered carbon atoms melt high and those of even carbon atoms low, just the opposite of the normal and *iso* series. An examination of the structural formulas, representing the aromatic residue by X, would seem to indicate that only the longest carbon chain, namely, that included in R, attached to the "key" carbon atom (designated by a star) affects the melting point. The fact that the isopropyl ester has an extremely high melting point is probably due to the presence of two identical units, the methyl group, on the key carbon atom, resulting in a highly symmetrical arrangement.



$$X\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O\text{—}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{}^*\text{—}R$$



$$X\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O\text{—}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{}^*\text{—}R$$

Experimental

3,5-Dinitrobenzoic acid, m. p. 203–205°, was converted into the acid chloride and this treated with about 10% excess of the alcohol, according to the directions given by Mulliken[13] with the following slight variations. In the case of the secondary alcohols the temperature was raised to 85–90° and the time of treatment increased to thirty minutes. The ester was extracted with a mixture of five parts of petroleum ether and

TABLE I

MELTING POINTS OF ALKYL ESTERS OF 3,5-DINITROBENZOIC ACID

Alcohol	M. p. (corr.), °C.	Melting points from literature	Alcohol	M. p. (corr.), °C.	Melting points from literature
Methyl	107.8	107.5;[13] 109;[15] 110–110.5;[14]	*Iso*butyl	86.5	83–83.5;[12] 87–88[14]
		112[16]	Iso-amyl	...	61–62[14]
Ethyl	92.7	90;[17] 91;[18,19] 92–93;[13]	Isohexyl	69.8	......
		93–94;[14] 94[16,20]	*Iso*heptyl	54.5	......
n-Propyl	73.0	73–73.5;[13] 74–75[14]	Iso-octyl	58.3	......
n-Butyl	62.5	61–63[14]; 64;[13] 61[19]	*Sec*.-propyl	122.1	121–122[14]
n-Amyl	46.4	....	*Sec*.-butyl	75.6	......
n-Hexyl	58.4	60–61[14]	*Sec*.-amyl	62.1	......
n-Heptyl	46.9	4748.5[14]	*Sec*.-hexyl	38.6	......
n-Octyl	60.8	61–62[14]	*Sec*.-heptyl	49.4	......
n-Nonyl	52.2	....	*Sec*.-octyl	32.2	......
n-Decyl	...	56–57[14]	*Sec*.-nonyl	42.8	......

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[13] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons Inc., New York, 1914, Vol. I, pp. 166 ff.

[14] Reichstein, *Helv. Chim. Acta.* 9, 802 (1926).

[15] Curtius, *J. prak.* Chem. [2] 76, 248 (1907).

[16] Herre, Ber. 28, 595–596 (1895).

[17] Staedel, Ann., **217,** 196 (1883).

[18] Beilstein and Kurbatow, *ibid.,* 202, 222 (1880).

[19] Brill, THIS JOURNAL, 43, 1323 (1921).

[20] Hiibner, Ann., 222, 79 (1884).

one part of ethyl ether, in which free acid and acid chloride are only very slightly soluble. The solvent was allowed to evaporate and the residue recrystallized to a constant melting point from 95% ethyl alcohol. Final melting points were taken with Anschütz thermometers graduated in tenths of a degree, for which certificates of the Reichsanstalt were available. These melting points were determined in the ordinary way with finely drawn out tubes of about one mm. diameter. A large glass tube equipped with a rotary stirrer of the paddle wheel type, driven at high speed by a small motor, was employed as a bath. This in turn was encased in a still larger tube whose corresponding dimensions were 1.0–1.5 cm. larger, the intervening air-bath serving to insure more even heating, this being carried out with a micro flame. To the mean of the final melting point range, in no case over 0.4° and in most cases 0.2° or less, were added the proper stem and tabular corrections, the figure to the nearest 0.1° being taken as the true value of the melting point. For brevity, only final corrected melting points are given. Included with these in the accompanying table are melting points obtained from the literature of such of these esters as have been previously reported.

The sources of the various alcohols were as follows. The methyl, ethyl, n-propyl, *iso*propyl, n-butyl, secondary butyl and isobutyl alcohols were cut sharply from good commercial grades on high precision stills, boiling point ranges being 0.2–0.3° and agreeing with accepted values. Normal and secondary octyl alcohols were supplied by the Eastman Kodak Co. and redistilled. The remaining alcohols were synthesized by the Grignard reaction; boiling points of the higher alcohols are:[21] *n*-amyl 137.8_{760}; *n*-hexyl 156.1_{758}; n-heptyl 176.0_{755}; n-octyl 195.3_{765}; n-nonyl 213.5_{758}; *sec.*-amyl 119.3_{760}; *sec.*-hexyl 139.7_{759}; *sec.*-heptyl 158.5_{754}; *sec.*-octyl 180.3_{765}; *sec.*-nonyl 198.2_{760}; *iso*hexyl 151.7_{758}; isoheptyl 169.5_{735}; *iso*-octyl 188.0_{767}.

Summary

The 3,5-dinitrobenzoates of twenty saturated aliphatic alcohols have been prepared.

Certain regularities have been observed in their melting points.

BALTIMORE, MARYLAND

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[21] The normal and secondary hexyl, heptyl and nonyl alcohols were synthesized in 200–300 g. quantities by L. M. Ellis, Jr., and R. F. Deese, Jr., and carefully purified for an accurate determination of physical constants to be published by them later. Boiling points given for these alcohols were determined by Ellis.

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

THE DIRECT INTRODUCTION OF SULFUR INTO AROMATIC HYDROCARBONS[1]

BY H. B. GLASS[2] AND E. EMMET REID

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Sulfur, in the presence of aluminum chloride, reacts with benzene to give thiophenol, diphenyl sulfide and diphenylene disulfide.[3] The same products are obtained by the dry distillation of the sodium salt of benzenesulfonic acid.[4] Since sulfur may be introduced into benzene by the use of a catalyst at low temperatures it was thought that at elevated temperatures this could be accomplished without the aid of a catalyst. Accordingly, the action of sulfur on benzene and ethylbenzene was investigated.

Results and Discussion.—Benzene and sulfur when heated together at 350° for twenty-four hours gave thiophenol, diphenyl sulfide, diphenyl disulfide, diphenylene disulfide (thianthrene) and hydrogen sulfide. It has been shown that diphenyl disulfide is obtained by heating thiophenol with sulfur,[5] and that this is decomposed on further heating to give diphenyl sulfide and free sulfur.[6] Diphenylene disulfide is formed by heating diphenyl sulfide with sulfur.[7] From the fact that thiophenol is obtained from sulfur and benzene, with the aid of a catalyst, it is probable that this is the first product formed at high temperatures without the aid of a catalyst. The formation of all other products isolated can be accounted for by the action of heat and sulfur on this one product.

The action of sulfur on ethylbenzene is quite different from that on benzene and much more rapid. When oxygen is passed into ethylbenzene, acetophenone is formed.[8] By analogy the action of sulfur should be such as to give thioacetophenone and hydrogen sulfide; no thio-ketone, however, was detected in the reaction mixture. Instead there was isolated a good quantity of 2,4-diphenylthiophene, this being the only sulfur-containing product, other than hydrogen sulfide. Baumann and Fromm[9] have shown that thioacetophenone polymerizes readily to give tri-thioacetophenone and that this is both depolymerized and decomposed on heating, anhydro-trithioacetophenone and 2,4-diphenylthiophene being

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[1] Presented in part at the Detroit meeting of the American Chemical Society, September, 1927.

[2] Du Pont Fellow in Chemistry.

[3] Friedel and Crafts, *Ann. chim. phys.*, [6] 14, 438 (1888).

[4] Stenhouse, *Ann.*, 149,252 (1869).

[5] Holmberg, *ibid.*, 359, 83 (1908).

[6] Graebe, *ibid.*, 174, 189 (1874).

[7] Krafft and Vorster, *Ber.*, 26, 2813 (1893).

[8] Stephens. THIS JOURNAL, 48, 2920 (1926).

[9] Baumann and Fromm, *Ber.*, 28,890, 895,907 (1895).

formed. Further, they have shown that anhydro-trithioacetophenone decomposed on heating to give styrene and 2,4-diphenylthiophene, and that styrene may react in either of two ways to give ethylbenzene or 2,4-diphenylthiophene. Diphenylthiophene, being a comparatively stable compound, when once formed does not undergo further change, while the other above-mentioned compounds readily decompose on heating. It is for this reason that the only sulfur-containing compound obtained from the reaction was diphenylthiophene, the analogy, however, of sulfuration to oxidation being supported.

Experimental

Benzene and sulfur were heated in a steel bomb, of 100-cc. capacity, at 350° for twenty-four hours.[10] Upon opening the bomb much hydrogen sulfide escaped and within the bomb there was a brown oil having the odor of thiophenol. On distillation of this oil there was obtained a small fraction boiling between 76 and 90" and a smaller fraction boiling between 140 and 175°. These two fractions were redistilled several times, thus obtaining unchanged benzene and thiophenol. The latter was identified by its lead mercaptide (calcd., Pb, 48.7; found, Pb, 48.8). That portion of the reaction product boiling above 175° was distilled at a pressure of 5 mm., a mixture of an oil and a solid coming over between 120 and 210" which gave no clear-cut fractions. The residue was a hard, black, glass-like tar. Most of the distillate went into solution on treatment with cold, absolute alcohol but there remained a white solid, difficultly soluble in hot alcohol, which after several recrystallizations gave a melting point of 156 5°. With hot concentrated sulfuric acid this solid gave an intense purple coloration and was identified as diphenylene disulfide (thianthrene) by a mixed melting point with a known sample.

The alcoholic solution from above was concentrated by boiling and cooled to −10°, a white solid separating out which was filtered while still cold. This solid, after recrystallization several times from alcohol, melted at 60°, and on treatment with dilute hydrochloric acid and zinc dust gave at once the odor of thiophenol; sulfur analysis gave 29.5% of sulfur (calcd. sulfur for diphenyl disulfide, 29.4%). It was thus identified as diphenyl disulfide. Vacuum fractionation of the residue from the above alcoholic solution gave an orange-colored liquid having a boiling-point range of 180–185° at 5 mm. This substance was identified as diphenyl sulfide by oxidation to the sulfone, melting point 127.5–128°.

The bomb leaked to some extent as shown by the fact that a piece of paper soaked in lead acetate solution placed above it during heating turned very black. From 50 g. of sulfur and 39 g of benzene there were obtained: 6.3 g. of hydrogen sulfide (absorbed in lead acetate solution and weighed as the sulfide); 8.6 g. of unchanged benzene; 1.8 g. of thiophenol; 27.8 g. of a mixture of diphenyl sulfide, diphenyl disulfide and diphenylene disulfide; 22.1 g. of tar; a total of 66.6 g. The loss was 22.4 g.

The sulfide and disulfide seem to be formed in about equal quantities (molal) while the amounts of thiophenol and diphenylene disulfide are about equal and are about half as great as those of the sulfide and disulfide.

It was thought possible that the iron of the bomb was acting as a catalyst for the reaction. A mixture of benzene and sulfur, in the same proportions as used in the bomb, was sealed in a glass tube and this placed in the bomb, surrounding it with ben-

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[10] For a description of the bomb and method of temperature control, see the paper by Herndon and Reid, THIS JOURNAL, 50,3086 (1928).

zene to equalize the pressure. The identical reaction took place in the glass that had taken place in the steel.

Sulfur and **Ethylbenzene.**—For this reaction a much larger bomb, of a capacity of 800 cc., was employed than that used for benzene. Ethylbenzene (4.1 moles) and sulfur (6.2 moles) were placed in the bomb and heated at 340–350" for forty minutes, at which time a small leak in the bomb head developed and heating had to be stopped. When the bomb had cooled down to room temperature there remained a pressure of 1200 lb. per sq. in. in it. The bleeder valve was opened and 78 g. of hydrogen sulfide was removed. The leak was repaired and the bomb again heated at 340–350°, this time for four hours, at the end of which time a serious leak developed in the brass bleeder valve and heating had to be stopped. Hydrogen sulfide at high pressures seems to attack the brass threads of the valve very rapidly. This second leak caused a large loss in material.

There was removed from the bomb 378 g. of liquid containing a small amount of solid. The solid was filtered off and the liquid distilled, about **5** cc. coming over between 30 and 40", at which point the temperature of the distilling vapors jumped rapidly to 130". There was obtained 126 g. of liquid boiling between 130 and 145°, at which point the vapors became slightly yellow and the distillation was stopped. This liquid consisted chiefly of ethylbenzene, but contained a small amount of styrene in as much as it decolorized a small amount of bromine very rapidly. The residue in the distilling flask, along with the solid filtered from the original reaction mixture, was extracted with hot alcohol; this solution on cooling deposited 86.5 g. of a light yellow crystalline substance, which on recrystallization gave a melting point of 119.5–120.5". On analysis it was found to contain 13.4% of sulfur; with concentrated sulfuric acid and isatin it gave an intense green-blue coloration. It was thus identified as 2,4-diphenylthiophene (calcd. sulfur, 13.56%).

Summary

Benzene reacts with sulfur at 350° to give thiophenol, diphenyl sulfide, diphenyl disulfide, diphenylene disulfide and hydrogen sulfide. In the case of ethylbenzene the side chain is the point of attack and 2,4-diphenylthiophene is the final product.

BALTIMORE, MARYLAND

[CONTRIBUTION PROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 6091

CHARACTERIZATION OF CERTAIN STARCHES AND THEIR AMYLOSES[1]

BY T. C. TAYLOR AND R. P. WALTON

RECEIVED JUNE 3, 1929 PUBLISHED NOVEMBER 8, 1929

In pursuing further the study of starches of various genera, we have followed two main channels of investigation. The one has had for its purpose the characterization of a starch as a function of its constituent amyloses; the other, a search for those chemical properties that would give us more rigid definitions of the amyloses themselves. All the work in this Laboratory is based primarily on the assumption that the organized starches are heterogeneous materials, the two principal components being designated as a- and β-amylose. This nomenclature corresponds approximately to that of Arthur Meyer.[2] From this point of view the amyloses are not to be considered as degradation or scission products and do not correspond to the types of amyloses obtained by Pringsheim through the action of B. *Macerans*, to those obtained by Pictet through the action of heat or to those obtained by Ling and Nanji through the action of enzymic agents.

Part I. Ratio of Amyloses in Wheat and Tapioca Starches

This consideration that starch granules are composed of different chemical substances rather than one homogeneous material was first definitely advanced by Raspail[3] in 1525. In his report a soluble and an insoluble fraction exhibited different colorations with iodine. The conception of differing chemical individuals was immediately challenged by some experimenters and defended by others. Since that time fully a hundred major investigations have been devoted to the problem of separating and characterizing these components. Specific reference need not be made here to the various observations and hypotheses which have been communicated, as a complete review of this literature has been published recently.[4]

The most obvious feature to be noted in a review of these earlier communications is the marked divergence in the reported ratios of the two or more materials. This might naturally be expected in that there are no precise definitions for these components and in all methods of separa-

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[1] The work covered in this paper is taken from a dissertation presented by R. P. Walton to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] A. Meyer, "Untersuchungen über die Stärkekorner," Jena, **1895.**

[3] Raspail, *Annales des sciences naturelles*, 6,224–239, 384–427 (1825).

[4] Walton, "A Comprehensive Survey of Starch Chemistry," Chemical Catalog Co., New York, **1928.**

tion it is necessary first to get these materials out of the granule, an end not easily accomplished by the ordinary hot water treatment most generally used.[5]

In the last few years, however, the ratios of the amyloses in a given starch reported by various workers have been more generally consistent.

The method of separation used in this Laboratory[6] has been so chosen because it is believed that interference due to unbroken or partially broken granules is eliminated, because fairly concordant results may be obtained easily and because the products have reasonably definite characteristics. The previous separations in this Laboratory gave ratios for the amyloses in corn, rice and potato starches. In this work separation studies have been carried out on wheat and tapioca starches because of certain specially significant characteristics of these common starches.

Experimental

The preliminary treatment with boiling alcoholic hydrochloric acid, as prescribed by Taylor and Iddles, was found to be too drastic for the starches used in this investigation. Treatments with alcoholic hydrochloric acid at 40–50° for one-half to one hour were usually sufficient to furnish starches which gave a relatively fluid paste upon subsequent thiocyanate gelatinization. The original purpose of this treatment was the removal of nitrogenous impurities, although it also serves to lower the viscosity of the resulting gelatinization mixture.[5] The granules remain intact, as shown by microscopic examination, although there are evidences of incipient rupture. When all starches thus far investigated are so treated and later gelatinized with hot water, a relatively thick paste is obtained, except in the case of wheat starch.

Wheat Starch.—Two hundred and fifty grams of air-dried starch was made into a paste with 170 cc. of alcohol, mixed with 150 cc. of alcoholic hydrochloric acid and mechanically stirred for one hour at 50° The concentration of alcoholic hydrochloric acid corresponded to 0.08 g. of hydrochloric acid per cc. of alcohol, as determined by titration. The alcoholic hydrochloric acid was removed by suction filtration and the starch washed free of hydrochloric acid by successive additions of fresh alcohol. The starch thus treated was introduced slowly into a large mortar containing 90 g. of ammonium thiocyanate in a solution of 450 cc. of water and 120 cc. of alcohol. After grinding for one hour at 45–50°, the solution became fluid and translucent. Microscopic examination indicated complete disruption of the granules. The gelatinized starch was thereupon precipitated from solution by alcohol and dehydrated by vigorous and prolonged grinding with absolute alcohol. After washing with ether and drying in air, 178.2 g. (dry weight) was mixed with 300 cc. of alcohol. introduced into 4 liters of water at about 55° with vigorous stirring and the resulting suspension placed in the usual apparatus[6] with a d c potential of 220 volts across the electrodes. Unless the gelatinized starch is introduced as an alcohol paste, bulky lumps will form which are difficult to break

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[5] Taylor and Beckmann, THIS JOURNAL, 51, 294 (1929).

[6] Taylor and Iddles, *Ind. Eng.* Ckem., 18, 713–717 (1926).

down. In the course of one or two weeks the combined effects of gravity and anodic migration caused a sharp separation of solid at the bottom of the jar, leaving an upper clear layer. The upper layer containing the soluble fraction (β-amylose) was siphoned off, fresh distilled water added and the procedure repeated until the upper layer no longer gave an iodine coloration. Toward the end of the operation the fresh distilled water was first heated to a temperature of $50-60^\circ$ and the suspension stirred vigorously. The β-amylose was obtained from the clear solution by precipitation with alcohol. The insoluble fraction (a-amylose) was collected on a suction filter and dehydrated with a current of air at 100° for about five days.

Tapioca Starch.—The same technique was used as before. The behavior is different from that of wheat starch in that the first downward movement of the boundary layer is somewhat slower. Toward the end of the procedure, however, the effect of the electrical potential is very marked. If the electrodes are reversed a sharp upward movement of the boundary layer may be noted. Also, the physical consistency of the alcohol precipitate differs from that obtained with wheat starch. With the latter the precipitate was mealy and easily ground with alcohol, although with tapioca starch the product was stiff and more difficult to dehydrate with alcohol.

Corn Starch.—Separations of the amyloses from corn starch were made in order to obtain products for the subsequent nitrations. Dehydration was effected by heating on a steam-bath with an excess of benzene and absolute alcohol.[5] The alcohol precipitate from the gelatinization mixture had the same consistency as tapioca starch.

While not of any unique significance, the record of the electrophoretic treatments is given in Table I. It serves to show that with the potential employed the separation is not fast and that repeated washing is necessary in order to accomplish complete separation.

TABLE I

RECORD OF ELECTROPHORETIC SEPARATION

Starch	Tapioca	Tapioca	Tapioca	Wheat	Wheat
Sample no.	1	2	3	1	2
Dry gelat. starch in 4 liters of water, g.	299	138	133.1	178.2	167.4
Electrodialysis, days	48	24	28	46	36
Changes of dialysis water	14	10	11	17	10

In Table II the amount of a-amylose as separated by this method is given for two starches not heretofore investigated.

TABLE II

α-AMYLOSE IN TAPIOCA AND WHEAT STARCHES

Starch	Tapioca	Tapioca	Tapioca	Wheat	Wheat
Sample no.	1	2	3	1	2
α-Amylose, g.	52.4	22.5	21.9	42.5	39.5
α-Amylose, %	17.5	16.3	16.4	23.8	23.5

The specific rotations of the soluble or β-amyloses from these starches are given in Table III.

TABLE III

OPTICAL ROTATIONS OF β-AMYLOSES AT 25°

Sample	Wheat No. 1	Wheat No. 2	Tapioca No. 2
Concn., g./20 cc. water	0.2032	0.4776	0.3728
Angular rotation, 2-dm. tube	4.51"	10.67°	8.14°
Sp. rot. λ = 5461 Å.	221.2"	223.4"	218.3"
Sp. rot. λ = 5892.5 Å.	186.9"	188.7"	184.4"

The factor (0.845) for converting readings with the green mercury line (5461 Å.) to the D sodium line (5892.5 Å.) was obtained by direct comparisons, using a concentrated aqueous solution of β-amylose. The lines were obtained from a continuous spectrum, patches of which having passed the spectroscope were chosen so that the optical center of each path had the desired wave length. The optical centers were determined by means of a quartz test plate calibrated by the Bureau of Standards. The procedure has been described by Levene and Bencowitz.[7] All β-amyloses gave the usual deep blue colorations with iodine–iodide test solutions.

From the results in Table II it is seen that the ratio of a- to β-amylose in the case of tapioca starch is approximately 17:83, the β-amylose being calculated by difference. Taylor and Iddles obtained practically the same ratio for corn and rice starches. The ratio of a- to β-amylose in the case of wheat starch is approximately 24:76 and indicates a higher content of a-amylose than any of the starches previously investigated by this method.

Part II. Characterization by Determination of Associated Non-Carbohydrate Materials

In the foregoing section it was stated that the particular method of separation used was preferred because of certain advantages in manipulative technique and because the separated products exhibited distinctively different characteristics which did not seem to be dependent merely upon the method of separation.

From the standpoint of physical behavior it has been found that P-amylose is fairly soluble and a-amylose relatively insoluble. β-Amylose passes through collodion membranes of a definite degree of permeability, whereas a-amylose is retained by the same membranes. β-Amylose does not migrate under the electrical potential imposed, whereas a-amylose exhibits a definite electro-negative behavior. As found previously for corn, rice and potato starches, these physical characteristics were likewise noted here in the case of wheat and tapioca starches.

The distribution of associated non-carbohydrate material, notably

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[7] Levene and Bencowitz, J. *Biol. Chem.*, 72, 627–634 (1927).

fatty acid residues and phosphate residues, has also been found previously to constitute a further basis of definition of the amyloses. This distribution accordingly was determined in these cases also and is reported in the following.

Experimental

Fatty acids were determined according to the method of Taylor and Nelson,[8] all analyses being run in duplicate. The results agreed within 2% for "fatty acids by hydrolysis." although determinations of "extraneous fat" were considerably less accurate and the extraneous fat extracted from some samples is negligible.

The acid number for the ether-soluble, fatty material liberated by hydrolysis was determined by titration with 0.05 N alkali, after dissolving the fat in hot alcohol previously neutralized to phenolphthalein. In the case of corn starch, Taylor and Lehrman[9] have shown that these fatty acids consist exclusively of palmitic, oleic and linolic acids, the combination giving an acid number of 186.

The results of the inquiry into the content of non-carbohydrates in these two newly investigated starches is given in Tables IV and V.

TABLE IV

DISTRIBUTION OF ETHER-SOLUBLE MATERIAL IN WHEAT AND TAPIOCA STARCHES

Sample	Wheat starch	Gelat. wheat	Wheat a-amylose		Tapioca starch	Tapioca α-amylose
No.	....		1	2	....	2
Extraction time, hours	3	7	6	6	5	10
Ether sol. mat., prelim. ext., %	0.031	0.063	Neg.	Neg.	0.048	0.015
Ether-sol. mat. after hyd., %	0.58	0.38	0.92	1.18	0.10	0.16
Acid no. of ether-sol. material	178.2	...	...	172.7	....	....

Phosphorus determinations were carried out according to the microanalytical method described by Pregl.[10] This is based on the previously developed method of von Lorenz[11] and consists in successive oxidation, acid digestion and precipitation as ammonium phosphomolybdate.

TABLE V

PHOSPHORUS DISTRIBUTION IN AMYLOSES

Sample (wheat)	No.	P expressed as P_2O_5, %	Sample (tapioca)	No.	P expressed as P_2O_5, %
Starch (untreated)		0.270	Starch (untreated)		0.137
Starch (gelatinized)		.224	a-Amylose	1	.068
a-Amylose	1	.353	a-Amylose	2	.059
a-Amylose	2	.265	β-Amylose	2	.041
β-Amylose	2	.041			

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[8] Taylor and Nelson, THIS JOURNAL, 42,1726–1738 (1920).

[9] Taylor and Lehrman, *ibid.*, 48, 1739–1743 (1926).

[10] Pregl-Fyleman, "Quantitative Organic Microanalysis," 1924.

[11] Von Lorenz, "Landwirtschaftlichen Versuchs-Stationen," 51, 183 (1910); Neubauer and Lucker, *Z.* anal. *Chem.*, 51, 161 (1912).

The phosphorus may be considered as non-dialyzable phosphate for the case of the a-amylases, in that they have been in contact with several changes of water over a period of about two months. This is not the case, however, for the whole starches or the β-amyloses.

From the fatty acid determinations given in Table IV it is evident that wheat starch is closely similar to those other cereal starches, corn and rice starch, characterized by Taylor and Iddles. A large proportion of the "fatty acids by hydrolysis" is retained by the starch even after complete disruption of the granule. Practically all the fatty acids of the whole starch are accounted for in the insoluble a-amylose fraction, separated by electrodialysis.

Tapioca starch, a tuber or root starch, likewise contains a definite amount of ether-soluble material, although in considerably smaller quantity. The insoluble a-amylose fractions in all cases contain an appreciably greater amount of fatty acid residues than the whole starch.

In the case of wheat starch it is evident that practically all of the combined phosphorus of the whole starch is contained in the a-amylose fraction. With tapioca starch the unusually low content of phosphorus makes such a conclusion somewhat hazardous, although it is reasonably safe to assume that here also practically all the combined phosphorus is contained in the α-amyloses.

The unusually low content of phosphorus and of fatty acids in tapioca starch may possibly be connected with its reported superiority in certain industrial processes. This starch has been considered by some operators as being the most suitable source material for the manufacture of alkali-starch adhesives, nitro starches and certain types of dextrin.

Part III. Characterization by Means of Derivatives

In Part II physical differences of starch components were described and differences in amount of associated non-carbohydrate materials were determined. In this section nitrate derivatives were prepared and characterized in a further attempt to define the amyloses. These nitrate esters were investigated as a continuation of the work of Taylor and Werntz,[12] in which the chemical behavior of the amyloses was studied in methylation and acetylation reactions. Also, the rather recent industrial prominence of starch nitrates as explosive materials lent interest to the study of these derivatives.

Nitration.—A number of investigators consider that starch is not subject to extensive degradation during the usual nitration processes. Brown and Millar[13] treated a starch nitrate with ammonium sulfide and hydrogen sulfide and demonstrated that the regenerated starch had the

[12] J. H. Werntz, "Studies of the Corn Amyloses," Columbia Dissertation, 1926,

[13] Brown and Millar, *J. Chem. Soc.*, **75,** 308–315 (1899).

same rotatory power as soluble starch. Béchamp[14] treated various starch nitrates with ferrous salts and also showed that the rotation of the regenerated starch was identical with that of soluble starch. Okada[15] regenerated with alcoholic ammonium hydrosulfide and demonstrated a low content of reducing material in the recovered product. All regenerated starches exhibited the characteristic deep blue iodine coloration. Commercial nitrations with "mixed acids" leave the starch granules practically unchanged in physical appearance.

On the premise that nitration does not involve profound degradation it was considered that a comparison of the optical rotations of the amylose nitrates might have a bearing on certain of the definitions given for amylose and amylopectin'' by Samec and Mayer.[17] According to their definition the molecular weights of amylose and amylopectin from potato starch are approximately 80,000 and 113,000 as determined by osmotic pressure methods. Also they report the optical rotation of amylopectin or rather its immediately solubilized succedent as being about 7° higher than that of amylose.

Should there be a relation of 2:3 in the molecular complexity of these components in common starches, it might be expected that uniformly prepared nitrate derivatives would also exhibit significant differences in rotatory power. In the following work, however, a fairly close agreement was obtained with the nitrates of the different amyloses from three starch varieties.

With respect to further possible chemical distinctions in the derivatives of the starch fractions, the recent communication of Friese, Smith and Hess[18] is of interest. They report that the solubilities of the triacetates of "amylopectin" and "amylose" from wheat starch differ qualitatively in the solvents chloroform, acetone, benzol and ethyl acetate, the amylopectin derivative being insoluble and the amylose derivative being fairly soluble. These fractions were separated by successive treatments of starch with hot water. The reported insolubility of the acetate, however has not been confirmed by the recent findings of Brigl and Schinle.[19]

In the following the uniform nitrate derivatives of the two fractions obtained from three different starches indicated no qualitative differences in solubility. This was noted with acetone, in which both are readily soluble, and in hot and cold alcohol, in which the solubility is comparatively slight.

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[14] Béchamp, *Ann. chim. phys.*, [3] *64,311444 (1862).*

[15] Okada, ***Cellulose Industry*** (Tokyo), 3, 3–14 (1927).

[16] "Amylose" and "Amylopectin" may be considered as corresponding approximately to the "β-amylose" and "a-amylose" of this Laboratory.

[17] Samec and Mayer, *Kolloidchem* ***Beihefte,*** 13, 272–288 (1921).

[18] Friese, Smith and Hess, ***Ber.,*** 61, 1975 (1928).

[19] Brigl and Schinle, *ibid.,* 62, 99–103 (1929).

Experimental

The method of Will and Lenze[20] was selected as being best adapted to the preparation of stable nitrates of fairly high nitrogen content and of sufficient uniformity. According to this procedure, oven-dried starch is dissolved in 10 parts (by weight) of cold fuming nitric acid (sp. gr. 1.52) and the nitrate precipitated by the addition of 20 parts of cold, concentrated sulfuric acid. The nitrating acids are removed by washing repeatedly with cold water and the lower nitrate derivatives by fractional extraction with hot alcohol. Further impurities are removed by dissolving the resulting nitrate in a mixture of acetone and alcohol and precipitating by evaporation of the acetone. The product is stabilized by boiling an aqueous suspension for at least twenty-four hours.

This latter treatment with boiling water is essential to the stability of the product, although the duration of the procedure may be shortened if a stabilizing treatment such as that recently proposed by Snelling[21] is used. This method involves suspending the nitrate in a boiling aqueous solution of sulfur dioxide and subsequently neutralizing with a small amount of ammonia. Unstable nitrates are supposedly reduced without affecting the more stable nitrates. Fairly good results were obtained by this method. The addition of stabilizing agents such as those used in industrial practice[22] was not resorted to because of the probability that such materials would affect the constants subsequently determined. A typical product prepared in these experiments showed a heat stability of twenty minutes at 135° with methyl violet test paper[23] and an explosion temperature of 182° when a 0.25-g. sample was heated in a test-tube at the rate of 2° per minute.

Starch nitrates are invariably decomposed on drying unless they have been subjected to some stabilizing treatment; even drying *in vacuo* at 50° initiates a steady decomposition involving the loss of nitrogen. This marked instability of starch nitrates has, until the last few years, prevented their successful application as commercial explosives, despite a number of very serious attempts in this direction.

In order to obtain strictly comparable nitration conditions, the temperature of the nitrating acid was maintained at 2–6° and the time of nitration made exactly two hours. This was sufficient to obtain practically complete solution of the materials nitrated. Occasional small lumps of undissolved starch nitrate were removed by filtering through glass wool. The method of Will and Lenze prescribes a twenty-four-hour treatment, which may explain the higher nitrogen content of their products. Introduction of the starch as a fine dust by means of an air jet was found to give good results, although this procedure was not used consistently.

Besides tapioca starch and potato starch, specially purified corn starch has been found suitable for large scale nitrations, Sadtler's preliminary purification treatment[24] being particularly satisfactory. This special treatment consists essentially in successively treating the starch with 2% aqueous sodium hydroxide and saturated bleaching powder solutions. Removal of fatty material is probably one of the principal purposes of this operation. That this material may be an interfering element is evidenced by the difficulty encountered when nitrating corn a-amyloses

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[20] Will and Lenze, Ber., 31, 68–90 (1898).

[21] Snelling, U. S. Patent 1,504,986 (1924).

[22] U. S. Patents 779,421, 875,913–875,928, 1,386,438, 1,462,074, 1,473,257.

[23] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1925, Vol. II, p. 1403.

[24] Sadtler, U. S. Patent 1,211,761 (1917).

in these experiments, a preliminary treatment with dilute alkali being necessary for successful nitration. Wheat α-amylose, however, was nitrated without the necessity of such a treatment, although clear solutions in acetone were obtained only when the material had been first washed with dilute alkali before the nitration.

Nitrogen was determined by decomposing the nitrate with alkali and alcohol, reducing with Devarda's alloy in alkaline solution and distilling the resultant ammonia into standardized acid as described by Kesseler.[25] The alcohol acts as a highly effective catalyst in the alkaline saponification of the nitrate ester. Analyses were run in duplicate, the results agreeing within 2%. The method was found to agree well with the micro-Dumas combustion method. Identical samples, for example, analyzed by this method and the micro-Dumas gave 12.22 and 12.12% of nitrogen, respectively. As noted by Kesseler and several other experimenters, determinations with the Lunge nitrometer were generally unsatisfactory because of the insolubility of starch nitrate in sulfuric acid.

A commercial starch nitrate prepared with "mixed acids" and still retaining the characteristic granular form of starch was included in the

TABLE VI

SPECIFIC ROTATIONS AND NITROGEN CONTENT OF NITRATED STARCHES AND STARCH COMPONENTS AT 25°

Material	N, %	Concn, g /50 cc of acetone	Angular rot, 2-dm tube	Specific rotation X = 5461Å Green Hg	X = 5892 5Å. Yellow Na
Tapioca β-Amylose	1 2 0	05916	3.34	1410	119.8
		.5032	2 86	142.1	120.8
Tapioca or-Amylose	12 2	.3764	2.10	139.5	118.6
		.2652	1.49	140.4	119.4
Tapioca starch	12 1	.3877	2 20	141.8	120.5
Corn No. 1 β-amylose	12 2	.3781	2.16	142.8	121.4
		.3568	2.05	143.6	122.0
Corn No. 2 β-amylose		.4242	2.44	143.7	122.1
		.5475	3.12	142.4	121.2
Corn α-amylose	12.0	.3245	1.86	143.6	122.1
		.3062	1.75	142.8	121.4
Corn starch (Sadtler treated)	11.5	.2263	1.29	142.5	121 1
		.4091	2.33	142.9	121.5
Wheat β-amylose	12.5	.3644	2.04	140.0	119.0
		.3259	1.84	141.1	119.9
Wheat or-amylose	11.8	.3064	1.68	141.7	120.4
		.3462	1.95	140.8	119.7
Commercial "Nitro-starch"	12 8	.6728	3.73	1385	117.7
		.4860	2 70	139.05	118.2
		.6897	3.82	138 8	118.0

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[25] Kesseler, Rohm and Lutz, *Z. angew. Chem.*, 35, 145 (1922).

determinations. The sample was subjected to preliminary washings with carbon tetrachloride and water.

Rotations with the green mercury line were converted to those of the yellow sodium line by means of the factor 0.849, determined with a spectroscope and calibrated quartz plate in the way mentioned previously for β-amyloses. Corrections were not made for ash content of the nitrates, which was ordinarily less than 0.20%.

The influence of degree of nitration on the corresponding rotatory power has been investigated by Béchamp, whose work constitutes the only previous report on the optical rotation of starch nitrates. Calculating the approximate relation of the wave length of light used in his experiments to the D sodium light, a rotation of $\alpha_{\mathrm{D}} = 142.0°$ is found to correspond to a mono-nitrate (6.7% of nitrogen), while a rotation of $\alpha_{\mathrm{D}} = 120.0'$ corresponds to a di-nitrate (11.1% of nitrogen). Accordingly for each variation of 1% in the nitrogen content of the whole there is an approximate decrement of 5° rotation. It is apparent that the nitrogen content of the products in the above table was of sufficient uniformity for the purposes of this experiment.

Conclusion.—From the close correspondence of solubilities and optical rotations of the nitrate derivatives of several different amyloses obtained in these experiments, it might be concluded that they are closely similar in molecular complexity. The observations obtained with these nitrate derivatives, however, do not help to delineate the chemical nature of the amyloses.

Acknowledgment.—Mr. Kaufman of the Stein-Hall Company and Mr. W. A. Nivling of the Huron Milling Company supplied the samples of starches used. Dr. L. W. Bass, of the Rockefeller Institute for Medical Research, assisted in the determination of relative rotatory dispersions. Dr. A. Elek, of the same institution, carried out the micro-analytical determinations of nitrogen and phosphorus. These favors have been gratefully appreciated.

Summary

1. The α- and β-amylose ratio, according to the method of Taylor and Iddles, was determined for wheat and tapioca starches.
2. Relative rotatory dispersions of β-amylose and starch nitrate were determined for the green mercury line and the yellow sodium line.
3. The distribution of the non-carbohydrate constituents, fatty acids and phosphate residues was determined for wheat and tapioca starches.
4. Physical characteristics of the nitrate derivatives of starch components and of whole starches were determined.

NEW YORK CITY

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

THE COMPOSITION OF CHOLLA GUM. I. THE ISOLATION OF *l*-ARABINOSE, *d*-GALACTOSE AND *l*-RHAMNOSE

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Until recently not much work has been done upon plant gums since the work of O'Sullivan[1] and Tollens.[2] It is only lately that they have come into a position of importance more in keeping with their significance. Butler and Creteher[3] have classed them as acid polysaccharides and, as the name suggests, they present a phase of carbohydrate chemistry quite distinct from that connected with starch and cellulose.

These substances occur in nature as the salts of a complex acid, the molecule of which seems to be built about a nucleus of uronic acids. The monosaccharides, arabinose, galactose and frequently rhamnose, are attached in such a manner that it is possible to hydrolyze off one kind of monosaccharide more or less completely under suitable conditions without detaching another kind. For example, arabinose may be removed almost quantitatively from cholla gum while a part of the galactose and virtually all of the rhamnose remain in combination with the acid nucleus. The galactose, in turn, can be hydrolyzed off while the rhamnose remains attached to the uronic acid group. In like manner mesquite gum[4] was found to release its arabinose while the galactose-uronic acid complex remained intact.

Whether these various monosaccharides are attached to the acid nucleus in long chains arranged in the order in which they are removed or whether the relative ease of hydrolysis depends on the nature of the linking which holds them to the nucleus, we cannot say as yet. Since the original cholla gum does not reduce Fehling's solution, all of the aldehyde groups must be involved in the linkings that hold the molecule together. All hydrolytic products reduce Fehling's solution but no product reduces it vigorously in the cold until after it is hydrolyzed in the autoclave, a procedure which removes the most difficultly hydrolyzable sugar, rhamnose. Evidently the aldehyde group of the uronic acid in the cholla gum is joined to the rhamnose by a glucosidic linking. The other linkings remain a subject of conjecture.

The occurrence and general properties have been described by Anderson and Sands.[5] The present communication describes work preliminary

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[1] O'Sullivan, J. *Chem. Soc.*, *45*, 41 (1884); *ibid.*, **59**, 1029 (1891); *ibid.*, **79**, 1164 (1901).

[2] (a) Flint and Tollens, *Ber.*, 25, 2917 (1892); (b) Widtsoe and Tollens, "Dissertation," Gottingen, **1899**; *Ber.*, 33, 132 (1900); *(c)* Tollens, *ibid.*, 41, 1788 (1908).

[3] Butler and Cretcher. THIS JOURNAL, 51, 1519 (1929).

[4] Anderson and Sands, *ibid.*, 48, 3172 (1926).

[5] Anderson and Sands, *Am. J. Pharm.*, **97**, 589 (1925).

to the determination of the structure of the molecule and includes the isolation of *l*-arabinose, d-galactose and *l*-rhamnose and the identification of d-galacturonic acid as the uronic acid present.

Cholla gum as it comes from the plant is not a single compound. When it was ground to pass a forty-mesh sieve, ethanol dissolved 1% of its weight. Although the gum has a light yellow color and a faint, not unpleasant odor, this alcoholic extract upon evaporation of the solvent, was dark brownish-red and highly odoriferous. A part of this extract was ether-soluble and a part could be saponified with alkali, showing that this fraction contained the lipins and the fat-soluble substances and was not carbohydrate. The remainder of the gum is carbohydrate in composition but can be separated into two fractions. After extraction with 140 times its weight of water during a period of forty-eight hours,[6] about one sixth of the total volume contained the greatly swelled, water-insoluble portion amounting to 80% of the gum, while the remainder was a slimy, opalescent solution containing the rest of the gum. This procedure gave an imperfect separation, it is true, but analysis of the two fractions showed them to contain the same components though in somewhat different amounts. The water-soluble fraction was nearly twice as high in uronic acid as the water-insoluble fraction, while the latter fraction contained practically all of the non-hydrolyzable, cellulose-like fraction of the gum.

Analysis of the gum on a water-free basis gave the following results: ash, 8.4%; uronic acid,[7] 11.5%; arabinose,[8] 53.2%; rhamnose,[9] 5.5%; galactose,[10] 8.4%.

[6] The gum was thoroughly mixed with 80 times its weight of water and allowed to stand for twenty-four hours. Three-fourths of the volume was siphoned off and replaced with water. After another twenty-four hours the supernatant liquid was again siphoned off and the very mobile suspension of water-insoluble material was concentrated by centrifuging.

[7] The uronic acid was determined by the method of Lefèvre: (a) Van der Haar, "Anleitung zum Nachweis, zur Trennung and Bestimmung der Monosaccharide und Aldehydesauren," Gebrüder Borntraeger, Berlin, **1920,** p. 71–76; (b) Lefèvre and Tollens, Ber., **40, 4513** (1907); (c) Tollens, *Z. physiol.* Chem., 61, 95 (1909); (d) Lefèvre, "Untersuchungen uber die Glucuronsäure," "Dissertation," Gottingen, **1907.**

[8] Pentoses were determined according to "Methods of Analysis," A. O. A. C., 1925, and calculated as arabinose. Since furfural is liberated from the uronic acid as well as from the arabinose during a pentosan determination, the arabinose in the substance under consideration had to be calculated by correcting the total amount of furfural phloroglucide for that which was derived from the acid. To our knowledge, the relationship between galacturonic acid and its furfural-phloroglucide production has not been determined, so for this purpose the factor given by Lefèvre, expressing the relationship between glucuronic acid and its phloroglucide production, was used [Van der Haar, Ref. 7a, p. 71]. The accuracy of such a method is questionable. Any error from this source together with that resulting irom the inaccuracy of the pentosan determination itself when applied to difficultly hydrolyzable substances must be kept in mind in consideration of data determined by this method.

General Procedure for Separating the Constituents of **Cholla** Gum.—In order to separate the constituents, the cholla gum was subjected to a series of hydrolyses. After the liberation of arabinose by hydrolysis at 80°, the partially degraded gum acid was turned into its calcium salt (calcium salt "A") and separated from the sugar. Calcium salt "A" was further hydrolyzed at 100° and the calcium salt of the still simpler acid (calcium salt "B") was separated from the galactose. Calcium salt "B" was next hydrolyzed in the autoclave and the calcium salt of the resulting acid (salt "C") was separated from the rhamnose. Details of the procedure follow.

Initial Hydrolysis of the Gum.—The gum was ground to pass a 40-mesh sieve and extracted with ethanol to remove the lipoid substances. One kilo was mixed with ten liters of 2% sulfuric acid, placed in three-liter flasks and heated for thirty hours in water-baths kept at 80°.[11] After hydrolysis there remained a residue of a cellulose-like substance amounting to 10% of the weight of the gum, which resisted further decomposition even in the autoclave at 120°. It was filtered off and discarded.

The solution was neutralized with calcium carbonate, decolorized with norit and the resulting almost colorless solution was concentrated in the presence of excess calcium carbonate in large evaporating dishes over the free flame.[12] At low volume it was filtered and concentrated to 45% solids. The sirup was poured into 3 to 4 times its volume of 95% ethanol, slowly and with vigorous stirring. The light yellow, curdy precipitate was filtered off and washed with hot 95% alcohol. To ensure the complete removal of any sirup that was occluded, the precipitate was dissolved in water and after diluting to 26% solids[13] it was poured into 3 to 4 times its volume of ethanol; it came down again as a flaky precipitate. This was washed with hot alcohol and then ether. It gave 286 g of powdery light yellow calcium salt "A."

Isolation of *l*-**Arabinose.**—Since any sugar which hydrolyzed off the gum remained

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[9] Methyl pentoses were determined by the method of Ellett and Tollens and of Haywood and calculated as rhamnose: (a) Ellett and Tollens, *Z. deut. Zuckerind.*, *42*, 19 (1905); (b) Haywood, Bulletin 105, U. S. Bureau of Chemistry, 1907, p. 112.

[10] Galactose was determined according to van der Haar, Ref. 7a, pp. 123–130. The total amount of mucic acid resulting from a determination represented that produced from the galacturonic acid present as well as that from the galactose. We have found no statement of the exact relationship between galacturonic acid and its mucic acid production, but Ehrlich obtained from tetra-galacturonic acid a yield of 70% or more of pure mucic acid [*Chem.-Ztg.*, 41, 198 (1917)]. Since galactose gives about 75% of its weight of mucic acid, van der Haar determined galacturonic acid by multiplying the weight of mucic acid by the same factor that was used to determine galactose (Ref. 7a, p. 336). In this work the total weight of mucic acid was converted to galactose by use of the table compiled by van der Haar, and this value minus the weight of galacturonic acid as determined by the method of Lefèvre was taken as the weight of galactose in the original sample.

[11] The acid concentration and time of hydrolysis here and in later instances were chosen as optimum after hydrolyzing samples of the gum and the various salts under a variety of conditions.

[12] Evaporation at reduced pressure was not feasible because of the tendency of the solution to foam.

[13] The optimum concentration of the salt solutions for precipitation with alcohol was, in all cases, the most concentrated solution that could be added to the alcohol and give the desired finely divided precipitate in place of droplets of sirup which would coalesce into a gummy mass and thus carry down sugar. The volume of alcohol used was sufficient to prevent coalescence of the flaky precipitate as the watery sirup was added.

dissolved in the alcohol, all filtrates and washings were combined, allowed to stand overnight to permit any calcium salt remaining in colloidal suspension to settle and then concentrated to 84–86% of solids. The sirup was thinned with 200 cc. of methanol,[14] cooled and seeded with arabinose. Crystallization began within an hour, but the sirup was allowed to stand in the refrigerator for a week with occasional stirring in order that as much of the sugar as possible might separate. Enough 95% ethanol was added to make the thick mass into a thin paste and the crystals were filtered off with suction. The sugar was washed by triturating it with a mixture of one part of glacial acetic acid and three parts of 95% ethanol and later with ethanol alone. This gave 250 g. of light-colored, fairly pure product.

When the mother liquor from the arabinose was evaporated approximately to dryness in *vacuo,* there remained 328 g. of a vitreous, dark red, transparent sirup. Analysis showed the presence of 5.3% of uronic acid, 7.7% of galactose, 3.7% of rhamnose and 4.7% of ash. These substances doubtless were present as a calcium salt of a complex acid resembling that in salt "A," which owed its presence to its appreciable solubility in alcohol. In addition the sirup contained arabinose to the extent of 34.4% or 113 g. However, the second crop of arabinose never amounted to more than a few grams. The procedure followed in the case of mesquite gum, namely, the purification of the sirup by the precipitation of a second crop of salts in order to permit the further crystallization of the sugar, failed in this case. Bertrand's method failed to give cadmium xylonate, and the sirup was not fermented by yeast, showing the absence of both xylose and glucose. Why the mixture resisted separation has not been determined.

Identification of **l-Arabinose.**—When the sugar referred to above was purified by the method of Anderson and Sands[4] it melted at 155–157° and in 4% solution gave a specific rotation of $[\alpha]_D$ $+101.9°$. The hydrazone, after recrystallization from 95% alcohol, melted at 150–151° with decomposition.[15] **A** portion of the sugar was oxidized with bromine to arabonic acid. The phenylhydrazide of this acid was a creamy white substance melting at 212–213° and having a specific rotation of $[\alpha]$ $+15.2°$ in 1% solution. Fischer[16] gave 215° as the melting point and Hudson[17] gave the rotation of the hydrazide of d-arabonic acid as $[\alpha]$ $-16.09°$. These facts, together with the fact that seeding with arabinose caused crystallization of the sirup, identified the sugar as arabinose.

Nature of Calcium Salt "A."—Analysis of the salt gave the following results: ash, 9.4%; uronic acid, 33.9%; arabinose, 5.5%; galactose, 5.1%; rhamnose, 27.9%.

The success with which the arabinose was removed by hydrolysis at 80° was evidenced by the reduction of the arabinose content from 53.2% in the original gum to 5.5% in salt "A." **A** rather large portion of the galactose was lost, however. The 5.1% of salt **"A"** corresponds to 14.5 g. of galactose, while the mother liquor left after the removal of the arabinose contained 25.3 g. of galactose. The high rhamnose content of salt, together with the small amount of rhamnose found in the mother sirup mentioned above (3.7%), indicated the success with which this sugar was left undisturbed. Evidently this salt was the calcium salt of fragments of the original gum molecules derived by the loss of the arabinose, a part of the galactose and possibly a little of the rhamnose.

Hydrolysis of Calcium Salt "A."—The 280 g. of calcium salt **"A"** was dissolved in

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[14] Methanol was more suitable for diluting this sirup than ethanol since the calcium salt which remained dissolved in the sugar fraction was more soluble in the methanol and consequently showed less tendency to precipitate as a gummy mass.

[15] Van der Haar, Ref. 7a, p. 145.

[16] E. Fischer, "Untersuchungen über Kohlenhydrate und Fermente," Vol. I, p. 329.

[17] Hudson, THIS JOURNAL, **39,** 462 (1917).

ten times its weight of 1% sulfuric acid plus enough sulfuric acid to precipitate the calcium and heated in the boiling water-bath for six hours. The solution was then neutralized with calcium carbonate, decolorized and evaporated in the presence of excess calcium carbonate. At low volume it was filtered, the concentration adjusted to 55% solids, and when cold the sirup was precipitated with ethanol as in the case of salt "A." The light yellow granular precipitate (calcium salt "B") amounted to 200 *g.*

Isolation and Identification of d-Galactose.—The alcoholic filtrates and washings obtained in the isolation of salt "B" were concentrated as much as possible *in vacuo* and then mixed with an equal volume of glacial acetic acid and seeded with galactose. Crystallization followed within a few minutes. After standing for a few days in the refrigerator, the galactose was filtered off and washed with a mixture of one part of glacial acetic acid and three parts of 95% alcohol. The yield of crude sugar was 18 g.[18] After purification[4] the product melted at 163–165°, gave a specific rotation of $[\alpha]_D$ 79.7° in 4% solution and produced approximately the quantitative yield of mucic acid when oxidized with nitric acid. These data identified the sugar as d-galactose.

Nature of Calcium Salt "B."—Analysis of this salt was as follows: ash, 9.5%; uronic acid, 40.8%; galactose, 0%; arabinose, 2.7%; rhamnose, 28.5%.

The hydrolysis at 100° appeared successful in the complete removal of galactose and, in view of the inaccuracy involved in the arabinose determination, the small percentage of that sugar found in salt "B" might as well be interpreted to indicate its absence as not. The fact that further hydrolysis of the salt in the autoclave left its pentose content unchanged substantiated the assumption that arabinose was completely removed from the gum by this second hydrolysis. The high rhamnose content of this salt, together with the fact that only 4.3% of rhamnose was found in the mother liquor from the galactose, showed that rhamnose was not conspicuously disturbed by hydrolysis at 100". Calcium salt "B" differed from salt "A" mainly in that galactose and the last remnant of arabinose had been removed from the molecule.

Hydrolysis of Calcium Salt "B."—One hundred ninety-five grams of salt "B," dissolved in ten times its weight of 2% sulfuric acid with a sufficient excess to precipitate the calcium, was hydrolyzed in the autoclave at one atmosphere gage pressure or 120° for eight hours. The solution was neutralized, decolorized, concentrated to 50% solids and the salts were precipitated with alcohol exactly as in the two preceding cases. Eighty-six grams of light brown calcium salt "C" resulted.

Isolation and Identification of *l*-Rhamnose Hydrate.—Again the alcoholic filtrates and washings were evaporated in *vacuo* to a very thick sirup and mixed with an equal volume of glacial acetic acid. Without seeding the sirup showed no evidence of crys-

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[18] The fact that the yield of galactose was larger than the total galactose content of salt "A" as shown by analysis is not surprising in view of the lack of reliability of the method used when applied to galactans in the presence of foreign material. Schorger found that one sample of galactan from the larch gave values of galactan content varying from 44.56 to 93.77%. Dore found that varying the sample of pure galactose from 0.2 to 2 g. caused the yield of mucic acid to range from 54 to 90%. Lippman has shown that foreign organic substances may prevent entirely the separation of mucic acid. In the work on mesquite gum in this Laboratory it was difficult to get the analytical results to shoa a total galactose content which equaled the galactose actually isolated from the gum. The application of the method to duplicate samples of the hydrolytic products of cholla gum gave results that checked within 2–3% and led to conclusions that seemed reasonable in the light of other experimental results. It was with these facts in mind that the results of these determinations were used in this article: (a) Schorger, J. Ind. Eng. *Chem.*, 8, 498 (1916); (b) Dore, *ibid.*, 7, 721 (1915); (c) Lippman, "Chemie der Zuckerarten," 3d ed., Vol. I, p. 274.

tallization at the end of three weeks, but upon seeding with rhamnose, crystals formed rapidly with the liberation of heat. After several days the sugar was filtered off and washed with the acetic acid–alcohol mixture. The yield was 27 g. The sugar was purified by dissolving it in water, decolorizing, concentrating to 86% solids and adding half its volume of glacial acetic acid. The sugar obtained melted at 92–94° and formed a phenylosazone which melted at 178–180°. In 4% solution the specific rotation was $[\alpha]_D$ $-5.1°$ after five minutes and $[\alpha]_D$ 0° after ten minutes, while the final constant value was $[\alpha]_D$ $+7.8°$. The sugar was thus identified as *l*-rhamnose hydrate.

Nature of Calcium Salt "C."—Analysis of the salt gave: ash, 17.0%; uronic acid, 36.1%; galactose, 0%; arabinose, 2.9%; rhamnose, 10.5%.

The rhamnose was incompletely hydrolyzed off but was reduced from 28.5% in salt "B" to 10.5% in salt "C." Therefore salt "C" approached very closely in composition the calcium salt of the nucleus of the gum. Work on the constitution of this salt as well as the salts "A" and "B" is in progress in this Laboratory. The destruction of the uronic acid during the vigorous hydrolysis required to remove the rhamnose was shown by its reduction from 81.6 g. in salt "B" to 31.1 g. in this final salt.

Identification of d-Galacturonic Acid.—The calcium salt "C" reduced Fehling's solution almost immediately in the cold and gave the naphthoresorcinol test, properties peculiar to the uronic acids. Oxidation with nitric acid produced mucic acid in amounts corresponding to the galacturonic acid as determined by the method of Lefèvre. When this salt was treated with bromine water in the cold, a white precipitate of mucic acid formed which was soluble in sodium hydroxide, reprecipitated upon acidification with hydrochloric acid and melted at 215°. When oxidized with bromine water at 100°, the salt yielded 17.7% of mucic acid, an amount corresponding in magnitude to 20.7% obtained by oxidation with nitric acid. Galactose will not give appreciable quantities of mucic acid when oxidized with bromine, whereas Ehrlich[19] found tetra-galacturonic acid to yield 60–70% of its weight of mucic acid. These facts proved that the uronic acid in cholla gum was d-galacturonic acid. The absence of glucuronic acid was established by failure to obtain potassium acid saccharate from the oxidation products of calcium salt "C."

Summary

1. Cholla gum, by a method of successive hydrolyses, was changed into salts of three distinct acids, each differing from its precursor in the loss first of arabinose, then galactose and finally rhamnose.
2. l-Arabinose, d-galactose and *l*-rhamnose hydrate were isolated and identified.
3. d-Galacturonic acid was definitely proved to be the uronic acid in cholla gum.

TUCSON, ARIZONA

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[19] Ehrlich, *Chem.-Ztg.*, **41**, 198 (1917).

[Contribution from the Chemical Laboratory of the State College of Washington]

SOME ALKOXY DERIVATIVES OF DIPHENYL OXIDE

By Carrol A. Doran[1]

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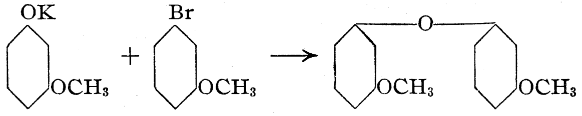
Since the stability of diphenyl oxide in the presence of alkalies has rendered compounds of this character valuable in soap perfumery, it seemed of interest to study the effect of substituents and especially of alkoxy groups on the properties of the compounds.

Ullmann and his co-workers[2] prepared diphenyl oxide by condensation of bromobenzene with potassium phenoxide, which required a temperature of 180–210° for a period of twelve hours. They found that by this method the yield was only 9% of the theoretical, but if a small quantity of metallic copper was used as catalyst, they were able to obtain a yield of 87%. o-Methoxy compounds were prepared by the same method.

Sabatier and Mailhe[3] prepared some mixed aryl ethers by the use of thorium oxide as catalyst. Weston and Adkins[4] prepared diphenyl oxide by treating phenol with metallic potassium and adding bromobenzene in the presence of a copper catalyst, heating the mixture to 210° for two hours.

The preparation of *m*-methoxydiphenyl oxides presented difficulties, as some of the intermediate compounds were not easily obtainable and did not condense as readily as the ortho or para compounds. In preparing the m-bromomethoxy and ethoxy compounds, preparatory to their condensation with alkoxy phenols to form the diphenyl oxides, the following steps were involved: nitrobenzene ⟶ *m*-bromonitrobenzene ⟶ *m*-bromoaniline ⟶ m-bromophenyldiazonium sulfate ⟶ m-bromophenol ⟶ *m*-methoxybromophenol. Phenols of the latter type were condensed with m-alkoxyphenols, which were prepared by the partial alkylation of resorcinol. The condensation apparently occurred as follows



A number of catalysts were used in attempts to improve the yield, under varying conditions of temperature and time, and optimum results obtained by the methods described.

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[1] Abstracted by C. M. Brewster from the thesis submitted by C. A. Doran to the State College of Washington in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

[2] Ullmann and Sponagel, Ber., 38, 2211 (1905); *J. Chem. Soc.*, 92, 38 (1907); Ullmann and Stein, Ber., 39, 622 (1906).

[3] Sabatier and Mailhe, *Compt. rend*, 155, 260 (1913).

[4] Weston and Adkins, This Journal, 50, 859 (1928).

Experimental Part

Choice of Catalysts.—Attempts were made to prepare the diphenyl oxide derivatives by the condensation of two phenols having other groups in meta position. While it was possible to prepare diphenyl oxide from phenol using aluminum chloride as catalyst, no condensation took place when the m-alkoxyphenols were used. When metallic potassium was used with *m*-methoxyphenol, and the resulting salt refluxed with m-metlioxybrotnobenzene in the presence of finely divided freshly reduced copper, only a trace of a high-boiling product resulted. Substitution of metallic sodium gave no better results, and in both cases a large amount of charring took place during addition of the metal to the phenol. Trials were also made with zinc chloride, concentrated sulfuric acid and freshly prepared thorium oxide on the mixed phenols, at temperatures ranging from 200 to 350°, but in no case did appreciable condensation take place. The most satisfactory method proved to be the condensation of potassium salts of phenols with the aryl halides at high temperatures, in the presence of finely divided freshly reduced copper as catalyst. This method gave fair results with bromo-alkoxy compounds but the chloro compounds gave much poorer yields.

Preparation of m-Bromo-aniline.—Nitrobenzene was brominated in the presence of powdered iron as catalyst. The product was fractionally distilled and crystallized from ether; m. p. 52.5". The m-bromonitrobenzene was reduced to m-bromo-aniline by the use of concentrated hydrochloric acid and stannous chloride, which gave an 85% yield. The speed of reaction must be controlled by cooling at the beginning, to prevent loss, and after the oil disappeared the mixture was refluxed vigorously for about thirty minutes. The solution was made alkaline, the oil extracted with ether, dried and distilled, giving a light brown product, b. p. 255–259°. Separation by steam distillation was not as satisfactory as extraction with ether.

Preparation of *m*-Bromophenol.—*m*-Bromo-aniline was diazotized and the product hydrolyzed to give m-bromophenol. The phenol could not be separated readily by steam distillation, due to formation of resins. The difficulty was overcome by carrying out the hydrolysis of the diazonium salt in an aqueous acid layer, under a benzene layer kept at its boiling temperature. The phenol derivative formed by hydrolysis was dissolved in the benzene layer as rapidly as it formed, and the final product was obtained by distillation of the benzene layer. No resinous by-products were formed and a yield of 76% of the m-bromophenol was obtained, b. p. 240–244°. The use of the benzene layer is a modification of a method of general application for prevention of resin formation in such reactions.

Preparation of *m*-Methoxybromobenzene.—The m-bromophenol was methylated by the method of Perkin, Ray and Robinson,[5] using dimethyl sulfate on the potassium salt. The mixture was refluxed on the steam-bath for one and a half hours, cooled, extracted with benzene, dried and distilled. The product had a boiling point of 218–221°; yield, 75%.

3,3'-Methoxydiphenyl Oxide.—To 4.1 g. of *m*-methoxyphenol[5] in an evaporating dish was added 1.9 g. of granulated potassium hydroxide, and the mixture heated to 90° until all solid potassium hydroxide had reacted. The temperature was then raised to 200° and the compound stirred for several minutes until the water formed during the reaction was driven off. There was a slight charring during this process. The dried potassium salt was then placed in a small flask with 6.2 g. of m-methoxybromobenzene and 0.1 g. of freshly reduced finely divided copper. This mixture was refluxed for six to seven hours at 300–320°; the temperature slowly rose as the reaction proceeded. The mixture was cooled, extracted several times with ether and the ethereal solution washed until the wash water showed very little color. The ether layer was dried over

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[5] Perkin, Ray and Robinson, J. *Chem. Soc.*, 945 (1926).

anhydrous sodium sulfate and fractionated, yield, 26%, giving a viscous oil of low surface tension, with a light brown color and a pleasant odor resembling that of diphenyl oxide; boiling point 332–334°; very soluble in benzene, ether or carbon tetrachloride; slightly soluble in alcohol or ligroin. It is not affected by aqueous potassium hydroxide solution and does not give a color reaction with ferric chloride in dilute alcohol.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.04; H, 6.09. Found: C, 73.07, 72.91; H, 5.97, 5.98.

3,3′-Ethoxydiphenyl Oxide.—*m*-Bromophenol was treated with ethyl sulfate and the mixture heated for five hours on the steam-bath; the yield of the *m*-ethoxybromobenzene was 85%; boiling point 228–231°. *m*-Ethoxyphenol was prepared by semi-ethylation of resorcinol; yield about 43%; boiling point 254–258°. The two monoethoxy compounds were condensed by treatment of the m-ethoxyphenol with solid potassium hydroxide and refluxing with m-ethoxybromobenzene in the presence of copper catalyst, as in the preparation of the dimethoxyphenyl oxide. The refluxing was continued for ten hours, the temperature slowly climbing to 350°. The ethereal extract when dried and fractionated gave a 36% yield of a pale brown liquid boiling at 341–344°; very soluble in benzene, ether, ligroin or carbon tetrachloride; only slightly soluble in cold alcohol. It is not affected by aqueous potassium hydroxide and does not give a color test with ferric chloride.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.42; H, 6.98. Found: C, 74.22, 74.28; H, 6.93, 7.04.

3-Methoxy-3'-ethoxydiphenyl Oxide.—This compound was prepared by treating m-methoxyphenol with solid potassium hydroxide and refluxing with *m*-methoxybromobenzene for eight hours in presence of the copper catalyst. Upon extraction and purification, a 20% yield was obtained, b. p. 338–341°. The compound has a light brown color and a pleasant odor. It is readily soluble in ligroin, benzene, ether or carbon tetrachloride and moderately soluble in cold alcohol. It does not react with potassium hydroxide solution and gives no color reaction with ferric chloride.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.77; H, 6.56. Found: C, 73.59, 73.66; H, 6.71, 6.52.

3,4′-Methoxydiphenyl Oxide.—*p*-Bromophenol was methylated, giving a 75% yield of the *p*-methoxybromobenzene, which was condensed with the potassium salt of m-methoxyphenol by refluxing for ten hours in the presence of the copper catalyst. The compound was separated by ether extraction and gave a yield of 30%; b. p. 336–338°. It is a light brown oil with a more pronounced odor than that of the 3-3'-alkoxy derivatives described above. It is less viscous but more soluble in alcohol than the 3,3′-methoxydiphenyl oxide. It is not affected by aqueous potassium hydroxide and gives no color reaction with ferric chloride. In order to determine whether the high temperature of the reaction had caused a rearrangement in position of groups the process was repeated as outlined above, except that the temperature of the reaction was never allowed to rise above 200°, as in the procedure of Ullmann.[6] The time of reaction was increased to thirty-five hours. There was no difference in boiling point between this compound and that formed at the higher temperature.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.04; H, 6.09. Found: C, 72.97, 73.17; H, 6.16, 6.05.

2,3′-Methoxydiphenyl Oxide.—o-Bromophenol was methylated by treatment with potassium hydroxide and dimethyl sulfate to form *o*-methoxybromobenzene; a yield of 45% was obtained. The latter compound was condensed with m-methoxyphenol by

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[6] Ullmann, Ber., 38, 2211 (1905).

treatment with potassium hydroxide and refluxing at 350° for ten hours in the presence of copper as catalyst. A yield of 33% was obtained, distilling at 326–329°. It has a pleasant odor, crystallizes in small cubical crystals which melt at 33–34° and is soluble in most solvents, though only slightly soluble in ligroin. It is not affected by potassium hydroxide in aqueous solution and gives no color reaction with ferric chloride.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.04; H, 6.09. Found: C, 72.82, 73.18; H, 6.14, 6.02.

Summary

1. Five new alkoxy derivatives of diphenyl oxide were prepared. They are compounds of great stability to alkalies or acids and to heat, of pleasant odor and of low surface tension.

2. In the preparation of phenols for condensation, a new method of procedure was discovered, namely, the hydrolysis of diazonium salts in hot acid solution under a layer of inert solvent, which prevents the formation of tarry by-products by removing the phenol from the acid hydrolyzing solution as rapidly as it is formed.

3. Of several catalysts used, finely divided freshly reduced copper gave the best yields.

PULLMAN, WASHINGTON

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

OMEGA-HYDROXY ALIPHATIC ACIDS. II. CONVERSION OF OMEGA-HYDROXYDECANOIC ACID TO CHAIN POLY-INTERMOLECULAR ESTERS AND TO A DIMERIC CYCLIC ESTER[1]

BY W. H. LYCAN[2] AND ROGER ADAMS

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In a previous paper a satisfactory method of preparation for many ω-hydroxy aliphatic acids was described. Attention was called to the fact that by the action of heat on such acids compounds were produced which appeared to be of high molecular weight. In this investigation these latter compounds are described in more detail. Several other reactions of w-hydroxy acids have been studied.

A recent paper by W. H. Carothers[3] has given a very clear exposition on polymerization: a proper definition, conditions of ring formation and an introduction to the theory of condensation polymers. The terminology in that publication has been adopted here. As pointed out in a general discussion by Carothers, bi-functional reactions may be either intramolecular or intermolecular. In the first case, the products will be monomeric

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[1] Lycan and Adams, THIS JOURNAL, 51, 625 (1929).

[2] This paper is an abstract of a thesis submitted by W. H. Lycan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Carothers, THIS JOURNAL, 51, 2548 (1929).

rings; in the second case the products will be polymeric rings or long chains. Intramolecular reaction takes place with readiness only when five- or six-membered rings are possible; whenever an intramolecular reaction would lead to rings of greater size, the reaction almost invariably proceeds intermolecularly with the formation of chain polymers.

The sole products of heating w-hydroxydecanoic acid alone or with solvents, with or without a catalyst, were chain poly-esters. A lactone was never detected among the products. The general structure of these high molecular weight compounds may be represented by the formula

$$HO(CH_2)_xCO_2—[(CH_2)_x—CO_2—]_n(CH_2)_x—COOH$$

The poly-esters were obtained as complex mixtures and crystallized from solvents as fine white powders. The crystals were less than microscopic in dimension but were definitely crystalline, inasmuch as sharp x-ray diffraction patterns were readily obtained.[4] The mixtures were, in general, soluble in the hot in acetone, alcohol, chloroform, benzene, toluene and ethyl acetate, but were only sparingly soluble in the cold. They were completely insoluble in water and ether.

The presence of the free carboxyl group in these molecules was demonstrated by the fact that their potassium salts were completely soluble in hot water. Furthermore, the exactly neutral potassium salt was perfectly stable in hot water, This was shown by the fact that a polymer recovered from its potassium salt by acidification with mineral acid had exactly the same properties and the same molecular weight as it had before neutralization. If ring compounds were present in the original polymer, either it would not be completely soluble in alkali or it would be partially hydrolyzed. In the latter event the recovered polymer might be expected to give a different average molecular weight determination, and different properties from the original polymer. There was no evidence that either of these things occurred.

The presence of a free hydroxyl group was also demonstrated beyond reasonable doubt. A polymeric mixture of average molecular weight of about 1100 yielded an acetyl derivative upon heating with acetic anhydride in boiling benzene. The fact that the average molecular weight of the product increased to about 1800 during the course of this reaction was not entirely unexpected. In addition to acting as an acetylating reagent the acetic anhydride might readily have acted as a catalyst for further intermolecular esterification. Intermolecular esters prepared in boiling benzene, using p-toluenesulfonic acid as a catalyst, had average molecular weights of about 2500. Thus the reactions of acetylation and further intermolecular esterification may be regarded as competing re-

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[4] Dr. G. L. Clark of the Chemistry Department of the University of Illinois has been kind enough to take x-ray photographs of some of these polymers. The detailed results will be published independently in a later communication.

actions. The acetyl polymer was characterized by its lower melting point (68–72° as compared to 74–76° for unacetylated derivative) and increased solubility in solvents. After hydrolysis with aqueous alkali and acidification with phosphoric acid, distillation yielded an acidic distillate. That this acetic acid could not have resulted from combination of the acetic anhydride with the free carboxyl group in the form of mixed anhydride is indicated by the increased molecular weight of the product. If it be assumed that acetic anhydride does not catalyze intermolecular esterification to a greater extent than *p*-toluenesulfonic acid, a decrease in average molecular weight would result from mixed anhydride formation.

The ordinary methods of molecular weight determination have never been extremely satisfactory for compounds of high molecular weight. In most cases the high polymers have not been sufficiently soluble in solvents to produce differences in boiling points, freezing points or vapor pressure large enough to permit of accurate measurement. Furthermore, it has not been possible to show that high molecular weight values thus obtained have not resulted from some kind of abnormal association in solution. Several attempts were made to determine average molecular weight values for a polymeric mixture, both by the boiling-point and freezing-point methods in benzene. The results varied from 1500 to 3000 in successive readings, and the same values could not be duplicated with any degree of accuracy. Average molecular weights were determined on the same material by titration of the free carboxyl group and these values never varied more than 5–8% from a mean of 2800. Inasmuch as free hydroxyl and free carboxyl groups often lead to abnormal molecular weights by the ordinary methods, it need not necessarily be inferred that the varying results obtained above are the limits of accuracy for other polymers.

The average molecular weights of these poly-esters were obtained easily by titration of the free carboxyl group. Large samples were titrated with fiftieth normal alkali solutions and from the values thus obtained average molecular weights were calculated. Inasmuch as the results of these titrations could be duplicated fairly closely with successive samples of the same mixture of polymers, it seems reasonable to assume that these were close approximations of the correct values. Furthermore, the values obtained from successively recrystallized samples increased in the regular manner expected; that is, the recrystallizations resulted in the concentration of the less soluble and more highly polymerized molecules. The filtrates yielded the more soluble fractions, which were constituted of fewer molecules of the parent acid, and the molecular weights determined for these fractions were characterized by a corresponding decrease. As the molecular weight of the polymer increased, the values obtained were subject to increased error. Even with polymers of average molecular weight as high as 9000, however, the error was not over 10%. The error in the values obtained for the lower polymers was ordinarily considerably less than 10%.

It has been previously intimated that the samples of poly-esters used for the molecular weight determinations were mixtures rather than individual compounds. It was impossible to obtain pure definite components from the highly complex mixtures in the reaction products because of the wide number of possible combinations and the similarity in solubility between each of them. The difference in solubility between a polymer constituted of twenty structural units and one constituted of ten is great enough to permit of separation, but when the mixture is made up of molecules containing every possible constituent from five or six to thirty structural units, separation becomes impossible. These mixtures were separated into fractions in which the components of each fraction were constituted of members of the same order of magnitude of structural units. However, the solubilities of the individual compounds of any one of these fractions were so similar that separation into individual components could not be effected. The molecular weight values observed, therefore, represent average values for a mixture constituted of a number of very similar components.

The addition polymers of Staudinger[5] result from equilibrium reactions and higher temperatures usually lead to lower polymers, whereas the poly-esters are formed by the elimination of molecules of water, and higher temperatures always lead to higher polymers. The lower temperature limit for the formation of polymers of ω-hydroxydecanoic acid without the presence of catalyst, was in the neighborhood of 100°. At any rate, heating the fused acid by itself at this temperature resulted in the formation of polymers composed of an average of between five and six structural units. Heating in a solvent required a somewhat higher temperature, perhaps because the alcohol–acid molecules were more widely dispersed. Heating in boiling toluene (b. p. 110°) over a considerable period of time resulted in only the very beginning of esterification. However, heating in cymene (b. p. 175°) resulted in a polymeric mixture of molecules constituted of an average of about six structural units. Other polymeric fractions were obtained by heating the fused acid over long periods of time at 200–210° and at 220–250°, respectively. The latter experiment produced polymers of average molecular weight of about 9000. In other words, these mixtures were composed of molecules constituted of in the neighborhood of fifty structural units.

[5] Staudinger *and* co-workers, *Helv. Chim. Acta.*, 5, 785 (1922); 7, 23, 842 (1924); 8, 41, 65, 67 (1925); **9,** 529 (1926); Ber., **53,** 1073 (1920); **57,** 1203 (1924); **59,** 3019 (1926); **60,** 1782 (1927); 61, 2427 (1928); 62, 241, 263, 442 (1929); **Ann.,** 447, 97, 110 (1926); Z. *physik. Chem.*, *126*, 426 (1927); *Kautschuk*, 237 (1927).

The use of *p*-toluenesulfonic acid permitted the reaction to proceed at a considerably lower temperature and resulted in a higher degree of poly-intermolecular esterification. The reaction proceeded smoothly in boiling benzene (b. p. 80°) with the production of a polymer of average molecular weight of about 2000. About the same results were obtained by its use in boiling toluene (b. p. 110°) but in cymene (b. p. 175°) polymers of much higher molecular weight mere formed.

A few words should be said concerning the nature of one of these reaction mixtures from any of the sources described. The original mixture might have, for example, an average molecular weight of 2000. This product would then be recrystallized repeatedly and samples titrated during the progress of their recrystallizations. The values obtained for the less soluble material continually increased, and after ten recrystallizations the average molecular weight would be in the neighborhood of 4000. The first few filtrates yielded samples whose average molecular weights were in the neighborhood of 1000. In other words, the mixtures all contained compounds constituted of a large number of degrees of esterification, and heating at increased temperature and the presence of a catalyst resulted in an increased predominance of the more highly esterified compounds.

The polymers obtained by these poly-intermolecular esterification reactions are obviously analogous to the natural "etholidcs" obtained by Bougault and Bourdier[6] from the waxes of a variety of conifers. These natural poly-esters were extracted from the desiccated leaves of the conifers with alcohol, and were purified by repeated crystallizations from the same solvent. As has been the case with their synthetic analogs, no pure components were isolated. They were characterized as being white powders and had, in general, the same solubilities that have been observed for the poly-esters of ω-hydroxydecanoic acid. These compounds yielded, upon hydrolysis, the two natural acids, juniperic and sabinic acids, mentioned in the previous paper.[1] It is entirely possible that both acids are combined in the single complex compounds which constitute the polymeric mixture. The following general structure was assigned to the polymer as a result of their experiments.

$$HO(CH_2)_x—CO[O(CH_2)_y—CO—]_nO(CH_2)_zCO_2H$$

Titration values indicated that the average molecular weight of the natural substances was between 1000 and 2000. The only products of complete hydrolysis were the alcohol–acids and the saponification numbers experimentally determined corresponded closely to the values calculated on this assumption. Furthermore, it was possible to prepare an acetyl derivative and the saponification number was modified an amount corresponding to the theoretical amount calculated, assuming the presence of one free hydroxyl group.

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[6] Bougault and Bourdier, *J. pharm. chim.* [6] 29, 561 (1909); [6] **30,** 10 (1909).

One anomalous fact presents itself with respect to the melting points observed for both the natural etholides and the synthetic polymers. Bougault and Bourdier recorded that, although they were unable to separate the natural mixture into pure definite compounds, they found that the melting points tended to group themselves around certain definite temperatures, namely, 68, 72, 78 and 82°. They assumed that this fact indicated that they were dealing with a mixture containing but a few components. It was found in these researches, however, that after the mixtures attained an average molecular weight of 2000, further increases in average molecular weight up to one of 9000 had no effect on the melting point. Every sample melted over 2° ranges between 74 and 77°. Several samples whose average molecular weights were of the magnitude of about 1000 melted over a range of only 2 or 3° around 65°.[6a] Bougault and Bourdier had recrystallized their etholides repeatedly before molecular weight determinations were made, so it is impossible to say whether or not the lower melting fractions also had lower average molecular weights.

The mixtures obtained from the conifers were composed of molecules constituted chiefly of a sixteen carbon and a twelve carbon hydroxy acid. The highest melting fraction, which had an average molecular weight of about 2000, melted around 80°. Since the two components, juniperic acid and sabinic acid, melt at 95 and 84°, respectively, it will be seen that the mixture melts considerably lower than either of the two component parent substances. This was true also in the case of the synthetic polymers of ω-hydroxydecanoic acid where the low fractions melted at 10° lower than, and the higher fractions at almost the same temperature as, the parent molecule.

An entirely satisfactory explanation of these facts does not present

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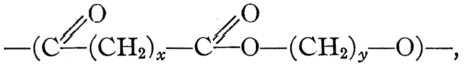
[6a] After the manuscript of this communication was in the hands of the printer, the article by Chuit and Hausser appeared [*Helv. Chim. Acta,* 12, 463 (1929)] entitled "Sur les acides-alcools polyméthylène-carboniques de 8 a 21 atomes de carbone." These authors have stated that upon heating ω-hydroxydecanoic acid at various temperatures, no definite products were obtained but merely mixtures of etholides of various size. After heating the hydroxy acid at 125° for ten hours they report that a material was isolated from the product which melted at 72.5–73°. The carbon–hydrogen analysis of this material indicated the presence of about six structural units in the molecule. All of the polymers studied and described in this communication which melted at approximately the point mentioned by Chuit were shown by molecular weight to contain ten or more structural units, while molecules of lower molecular weight (5–8 structural units) melted somewhat lower. As a consequence, Chuit's experiment was repeated and led to a product which melted at 74 to 76° and gave by neutral equivalent a molecular weight of about 2000 (12 structural units). Since minor details of experimentation frequently affect the size of the polymer materially, the difference between Chuit's results and those in this investigation may, probably, be accounted for in this way. Chuit found that ω-hydroxynonanoic acid gave entirely different results when subjected to polymerizing conditions. A careful comparison of the polymerization of the various ω-hydroxy acids is now under way in this Laboratory.

itself, Inasmuch as the polymers are mixtures, they might be expected to melt at lower temperatures than individual components of the mixture but, unfortunately, the latter may not be determined. The only plausible idea that suggests itself is based upon a consideration of the fundamental principle of the melting point. The temperature at which any substance melts depends only upon the forces operating between the molecules within the crystal. Whenever the temperature is sufficiently high to overcome these forces, then the substance fuses or melts. It is probable that any individual crystal of the poly-esters of w-hydroxydecanoic acid is composed of molecules constituted of unequal numbers of structural units. In fact the preliminary x-ray examination,[4] mentioned above, indicates this to be a fact. Other examples of the same phenomenon have been observed, particularly in the case of the polyoxymethylenes.[7] Inasmuch as the homologous molecules in each individual crystal are so similar, it may be assumed that the forces operating between two homologous molecules are of the same order of magnitude as those which would operate between two identical molecules. It must also be assumed that beyond certain limits of dimension of molecules, the magnitude of the operating forces is constant. If these two assumptions are correct, the melting points of the various fractions of the poly-esters might be expected to be constant. It is realized that this explanation is not entirely satisfactory, but more data are necessary before indulging in further speculation.

Carothers and Arvin[8] have prepared a large number of poly-esters by heating dibasic acids with glycols. The structure assigned to these compounds,  $—(\overset{O}{\overset{/\!/}{C}}—(CH_2)_x—\overset{O}{\overset{/\!/}{C}}—O—(CH_2)_y—O)—$, is very similar to that of the poly-esters of w-hydroxydecanoic acid. It is not surprising, therefore, that many properties are common to these two series of compounds. The various fractions of both series are crystalline, although this property is not highly developed in either case. The property of crystallinity in general seems to be more highly developed in these compounds where the recurring ester groups are separated by shorter carbon chains. Decamethylene sebacate, which is most similar in structure to the poly-esters of w-hydroxydecanoic acid, is described as a dusty powder which has a great tendency to become electrified. The same general description applies to the various fractions of the present series, and the tendency to become electrified is quite pronounced.

The solubilities of the two series are also somewhat similar. The polyesters produced from ethylene glycol and the lower dibasic acids such as succinic acid are the least soluble of those described by Carothers and Arvin. Decamethylene sebacate is more soluble and in this respect is

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[7] Hengstenberg, *Ann. phys.*, 84, **245** (1928).

[8] Carothers and Arvin, THIS JOURNAL, 51, 2560 (1929).

again more similar to the poly-esters of w-hydroxydecanoic acid. The previous authors point out that the behavior of their compounds on going into solution is indicative of the fact that the solutions are true molecular dispersions. This conclusion was drawn from the facts that solutions of their compounds in acetone, ethyl acetate, and glacial acetic acid were noticeably viscous only when fairly concentrated, and that the rate of solution was very rapid. The concentrated solutions of the poly-esters of ω-hydroxydecanoic acid were not at all viscous and solution in hot solvents was almost instantaneous. These compounds, therefore, present another group of substances of very high molecular weight which give normal solutions in contrast to the apparently colloidal solutions obtained from the polymers of high molecular weight of cyclopentadiene, isopropene and styrene.

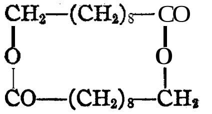
Carothers and Arvin also reported certain anomalies with respect to the melting points of their compounds. They found that the rate of heating had a marked effect on the melting point. Furthermore, they observed that the highest melting point obtained for any sample was within 5° of the lowest and that range was ordinarily within 2°. The effect of rate of heating on the melting points of poly-esters of w-hydroxydecanoic acid is not so pronounced but the short ranges and constancy for various fractions of the same material are similar. These phenomena have already been discussed. It is interesting to observe that the melting point recorded by Carothers and Arvin for decamethylene sebacate is 74°. This checks very closely the mean value of 74–76' obtained for all of the fractions of average molecular weights of between 2000 and 9000 of the poly-esters of w-hydroxydecanoic acid.

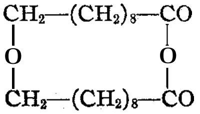
An acetyl derivative of w-hydroxydecanoic acid was obtained by the action of acetic anhydride on the pure acid. The reaction product consisted, in fact, of a mixture of the acetyl derivative of the acid with the diacetyl derivative of its anhydride. The diacetyl anhydride was readily converted to the acetyl derivative of the acid by shaking with water at ordinary temperatures. Although the free w-hydroxydecanoic acid could not be distilled at any pressure and temperature, its acetyl derivative was easily distilled without change under diminished pressures. In other words, the tendency to eliminate acetic acid from this molecule was considerably less than the tendency to eliminate water from its parent substance.

It has been pointed out that the bi-functional condensations present the possibility of proceeding either intramolecularly to form monomeric rings, or intermolecularly to form either chains or large rings. Carothers has pointed out that with dibasic acids and glycols ring formation occurred only when five- or six-membered rings could result. In a similar manner chain intermolecular esterification of w-hydroxydecanoic acid has been found to occur so readily that no cyclic compounds were isolated, It seemed, however, possible that if the chain intermolecular condensation could be inhibited, intramolecular or ring intermolecular condensation might occur. With this in mind, the potassium salt of ω-hydroxydecanoic acid was heated first with acetic anhydride and the product after removal of the acetic anhydride by distillation was dry distilled in a vacuum. If chain intermolecular condensation occurred the products would be non-volatile, not only because of their high molecular weight, but also because the potassium salt would be produced. On the other hand, the monomeric lactone produced by intramolecular condensation and the lower members of the products of ring intermolecular condensation might be expected to be volatile and could thus be isolated from the reaction mixture.

By carrying out the reaction as mentioned, a white crystalline material distilled, accompanied by a few drops of a high-boiling liquid. Traces of acetic anhydride and the few drops of high-boiling material were decanted from the crystals. These proved to be surprisingly pure, as shown by the sharp melting point, 95–95.5°, and by the fact that recrystallization did not alter this value. This substance by analysis and molecular weight determination corresponded to a dimeric lactone of Formula I.

I





II

Furthermore, it was readily saponified with aqueous alkali to yield ω-hydroxydecanoic acid, the original starting material. It also proved to be perfectly stable to water, inasmuch as it was recovered unaltered after shaking with water overnight. These latter two properties exclude the possibility that the compound may have a cyclic ether anhydride formula, II. It is impossible to say whether the dilactone results from the combination of two simple molecules or from the heat decomposition of higher chain polymers.

The dilactone is differentiated from the intermolecular chains by its higher melting point and greater solubility in solvents. It is, apparently, perfectly stable and reacts, in fact, as a normal ester.

The yields obtained in a number of experiments were approximately 5% of the theoretical amount and this value compares favorably with the yields obtained by Ruzicka,[9] in the preparation of large membered cyclic ketones. It should be pointed out that this is the second type of a very large ring which has been capable of direct preparation, and that it conforms to the present idea of the stability of large rings as embodied in the Sachse–Mohr theory.

Such a small amount of the high-boiling liquid accompanying the

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[9] Ruzicka, *Helv. Chim. Acta*, 9,249 (1926).

crystals has as yet been isolated, that a determination of its composition has not been effected. It appears to be a mixture and a preliminary examination has indicated that it is not a monomeric lactone. A mixture closely resembling this high-boiling material was obtained by the dry distillation of the potassium salt of ω-hydroxydecanoic acid itself. Apparently, no dilactone was formed during the course of this reaction.

Experimental

w-Hydroxydecanoic acid was chosen for the study of intermolecular esterification as it was the most readily available of the homologs previously described. It was found, in fact, that this acid could be obtained in yields of 65–75% of the theoretical amount, calculated from the weight of methyl undecylenate.

Intermolecular Esterification of ω-Hydroxydecanoic Acid.—The general method employed for the intermolecular esterification of w-hydroxydecanoic acid consisted in heating the acid alone at various temperatures and in various inert solvents at their boiling points, with and without a catalyst. Heating was continued from eight to sixty-five hours and chain poly-esters resulted. In the experiments where no catalyst was used, the products were recovered directly by merely cooling the fused mass or by cooling the solvent in ice and salt. When *p*-toluenesulfonic acid was used to catalyze the reaction the product was obtained as follows. The solvent was cooled in ice and salt, whereupon the product and catalyst separated together. The mixture was removed by filtration and sucked and pressed dry on the filter. The lumps were then crushed and powdered and suspended in a large excess of water at room temperature. After shaking vigorously for several minutes, the suspension was filtered and the product washed with many successive portions of water. It was then dried and an average molecular weight determination made. Both the products of the reactions wherein the catalyst was used, and wherein the acid was heated alone, were recrystallized repeatedly from successive portions of ethyl acetate and average molecular weight determinations were made at intervals during this process.

Molecular-Weight Determinations.—The average molecular weights of the various fractions were obtained by titrations. The general procedure employed consisted in dissolving a weighed sample (0.4–1.2 g.) of the poly-ester in 100 cc. of boiling alcohol which had been distilled over lime. Four drops of phenolphthalein indicator solution was added and an excess of fiftieth normal potassium hydroxide in 75% alcohol solution was run rapidly into the hot solution from a standard buret. About 100 cc. of cold water was added at once, and the resulting alkaline solution was back titrated with standard fiftieth normal aqueous potassium acid phthalate solution. It was found possible to obtain duplicate results within a maximum limit of 10%.

Intermolecular Esterification of ω-Hydroxydecanoic Acid in Boiling Benzene.—A 10-g. sample of w-hydroxydecanoic acid was recovered practically unchanged after heating in boiling benzene without a catalyst over a period of eight hours. When 0.2 *g.* of *p*-toluenesulfonic acid was added to a solution of 10 g. of the acid in 75 cc. of anhydrous benzene and refluxing was continued for twelve hours, a different result was obtained. To the resulting solution, 75 cc. of petroleum ether (b. p. 25–40') was added, and a fine white precipitate was obtained by cooling to −10°. After filtering and drying the product was powdered and suspended and shaken vigorously with 250 cc. of water at room temperature. It was filtered, washed in the filter with three additional 100-cc. portions of water and finally dried. The melting range of the dry polymer was 74.5–76.5" and titration gave an average molecular weight value of 2572.

The remainder of the product was recrystallized from 100 cc. of hot ethyl acetate.

This was accomplished by dissolving the material in 100 cc. of boiling ethyl acetate and cooling immediately in a flow of tap water of an average temperature of about 20°. The precipitate was filtered and dried and an average molecular weight determination made. To the filtrate was added 100 cc. of petroleum ether (b. p. 25–40°) and the resulting solution was cooled to −10°. In this manner additional polymer was recovered and another molecular weight determination made.

The main product was recrystallized four more times from ethyl acetate in the manner described and another average molecular weight determination was made. The combined filtrates from these recrystallizations yielded another fraction. The main product was again four times recrystallized from 100-cc. portions of ethyl acetate. An analysis for carbon and hydrogen and an average molecular weight determination were made on the 9-times recrystallized product. Table I will summarize the results of this experiment.

TABLE I

DATA ON RECRYSTALLIZED PRODUCT

	Times recryst.	Av. mol. wt.	Subs., *g.*	0.0158 N alk., cc.	0.0219 *N* acid, cc.	M. p., °C. (corr.)
1	0	2572	0.4456	15.2	1.9	74.5–76.5
2	1	3329	.4362	14.05	3.0	74.5–76.5
3	Filtrate	1047	.3085	23.85	3.3	62–66
4	5	3621	.6203	13.2	1.7	74.5–76.5
5	Filtrate	1474	.2426	12.9	1.8	34–51
6	9	4476	1.0812	19.6	3.1	74.5–76.5

Anal. Subs., 0.1805: CO_2, 0.4659; H_2O, 0.1771. Calcd. for $(C_{10}H_{18}O_2)_{26}\cdot H_2O = C_{260}H_{470}O_{53}$: C, 70.30; H, 10.52. Found: C, 70.39; H, 11.01.

Intermolecular Esterification of w-Hydroxydecanoic Acid in Boiling Toluene.—A 5-g. sample of ω-hydroxydecanoic acid was heated in 50 cc. of boiling anhydrous toluene for fifteen hours. The resulting product consisted chiefly of unchanged acid melting at 58–67°. This was shown by the fact that its neutral equivalent was 204 as compared with the theoretical value 180 for the pure acid. In a second experiment, 10 g. of w-hydroxydecanoic acid was heated in a boiling solution of 0.2 g. of *p*-toluenesulfonic acid in 75 cc. of anhydrous toluene through a period of sixty-five hours. The product was recovered and subjected to the same process as that obtained in the previous experiment with benzene as a solvent. In this experiment duplicate titrations were made on two fractions. In addition a sample of neutralized polymer was recovered from the neutral titration mixture by shaking with an excess of very dilute hydrochloric acid. This product was once recrystallized from hot ethyl acetate by cooling to −10° and a second molecular weight determination was made. The results are tabulated below. An analysis was made on a fraction obtained after five crystallizations.

TABLE II

ANALYTICAL DATA

	Times recryst.	Av. mol. wt.	Subs., g.	0.0158 *N* alk., cc.	0.0219 N acid, cc.	M. p., °C. (corr.)
1	0	2608	0.4362	18.9	6.0	75–77
	0	2409	.9918	34.1	5.8	75–77
Recov. from 1st 2 titrns.		2572	.8482	27.8	5.0	75–77
2	1	3443	.8392	21.6	4.45	75–77
	1	3268	.6412	18.1	4.1	75–77
3	5	4683	.6097	12.5	3.55	75–77
4	9	5563	.6893	12.0	3.0	75–77

Anal. Subs., 0.1835: CO_2, 0.4732; H_2O, 0.1807. Calcd. for $(C_{10}H_{18}O_2)_{27}\cdot H_2O = C_{270}H_{488}O_{55}$: C, 70.31; H, 10.59. Found: C, 70 33; H, 11.01.

A second experiment was conducted in which 10 g. of w-hydroxydecanoic acid was heated for thirteen hours in a solution of 0.2 g. of *p*-toluenesulfonic acid in 60 cc. of anhydrous toluene. The product was recovered in the same manner as in the previous experiments. The titrations were conducted as follows. The sample was dissolved in 100 cc. of alcohol which had been distilled over lime and the acid was directly titrated to phenolphthalein with twentieth normal alkali. The results of this experiment are summarized in Table III.

Table III

Results of Experiment

	Times recryst.	Av. mol. wt.	Subs., g.	0.0522 N alk., cc.	M. p., °C. (corr.)
1	0	2334	0 9019	7.4	72–76
2	1	2604	,7341	5.4	74–76
3	2	2846	,6613	4.45	74–76
4	3	3075	.6273	4.1	74–76

Intermolecular Esterification of **ω-Hydroxydecanoic** Acid in Boiling Cymene.—A 5-g. sample of w-hydroxydecanoic acid was heated in boiling cymene for ten hours. The product was recovered by cooling the solution to −10° and the cymene mother liquors were completely recovered by recrystallizing once from a 100-cc. portion of ethyl acetate. The dried material melted at 64–67°. An analysis for carbon and hydrogen and an average molecular weight determination were run.

Neutral equivalent. Subs., 0.2045: cc. 0.0158 *N* alk., 14.2; cc. 0.0219 *N* acid, 2.0. Neut. equiv., 1132.

Anal. Subs., 0.1806: CO_2, 0.4585; H_2O, 0.1719. Calcd. for $(C_{10}H_{18}O_2)_6\cdot H_2O = C_{60}H_{110}O_{13}$: C, 69.36; H, 10.59. Found: C, 69.24; H, 10.65.

A second experiment was conducted in which 10 g. of ω-hydroxydecanoic acid was heated in a boiling solution of 0.2 g. of p-toluenesulfonic acid in 75 cc. of anhydrous cymene. The product was recovered and treated in the usual manner and yielded the fractions recorded in Table IV. An analysis was made after five recrystallizations.

Table IV

Experimental Results

	Times recryst.	Av. mol. wt.	Subs , g.	0.0158 N alk., cc.	0 0319 *N* acid, cc.	M. p., °C. (corr)
1	0	5061	0 3381	5.2	0.7	73.5–74.5
2	1	7530	0.5324	6.0	1.1	74–76
3	5	7906	1.3938	15.9	4.6	74–76
4	9	8600	0.7312	8.9	2.4	74–76

Anal. Subs., 0.1575: CO_2, 0.4080; H_2O, 0.1564. Calcd. for $(C_{10}H_{18}O_2)_{46}\cdot H_2O = C_{460}H_{830}O_{93}$: C, 70.42; H, 10.59. Found: C, 70.65, H, 11.11.

Upon heating **ω-hydroxydecanoic** acid with p-toluenesulfonic acid in ether, the acid was recovered essentially unchanged.

Intermolecular Esterification of **ω-Hydroxydecanoic** Acid without ***a*** Solvent.—A ***5-g.*** portion of w-hydroxydecanoic acid was heated in a test-tube at 100° for ten hours under a pressure of 100 mm. **After** one recrystallization from ethyl acetate, the product melted at 63–67° and gave the following value for neutral equivalent.

Neutral equivalent. Subs, 0.4240: cc. 0.0158 *N* alk., 27.8; cc. 0.0219 N acid, 1.5. Neut. equiv., 1043.

A second sample of 10 g. of w-hydroxydecanoic acid was heated for ten hours at 200–210° in a test-tube. This product was recrystallized twenty times from 100-cc. portions of ethyl acetate after which it melted at 74–76" and gave a value of 6618 for average molecular weight.

Neutral equivalent. Subs., 0.9651: cc. 0.0158 N alk., 12.1; cc. 0.0219 N acid, 2.1. Neut. equiv., 6618.

A third experiment was conducted in which 10 g. of o-hydroxydecanoic acid was heated at 220–250° in a test-tube for fifteen hours. The material, upon cooling, was an amber-colored wax which could be readily recrystallized from ethyl acetate. The fractions obtained by recrystallizing this product are summarized in Table V. A sample was analyzed after the first crystallization.

TABLE V

ANALYTICAL AND OTHER DATA

	Times recryst.	Av. mol. wt.	Subs., g.	0.0158 *N* alk., cc.	0.0219 *N* acid, cc.	M. p., °C. (corr.)
1	0	5250	0.9241	12.8	1.2	...
2	1	7455	.5219	4.7	0.2	74–76
3	5	8733	.7772	6.9	.9	74–76

Anal. Subs., 0.1539: CO_2, 0.3968; H_2O, 0.1463. Calcd. for $(C_{10}H_{18}O_2)_{31}\cdot H_2O$ = $C_{310}H_{560}O_{63}$: C, 70.53; H, 10.59. Found: C, 70.32; H, 10.64.

An attempt was made to prepare poly-esters of higher average molecular weight by heating a fused sample of w-hydroxydecanoic acid with *p*-toluenesulfonic acid, but only charring resulted at 240°.

w-Acetoxydecanoic Acid.—Twenty grams of w-hydroxydecanoic acid was added slowly to 150 cc. of ice-cold acetic anhydride. There was no apparent evolution of heat during the addition. The solution was transferred to a 500-cc. round-bottomed flask and was stirred overnight. After heating at 90° for three-quarters of an hour, the resulting solution was distilled under diminished pressure. After the acetic anhydride and the acetic acid were removed, no constant boiling fraction was obtained, but the entire product distilled from 190–220° (1 mm.) and solidified in the receiving flask. It had a pleasant, fruit-like odor and did not lend itself to crystallization from any of the variety of solvents. An analysis indicated the probability that the product consisted of a mixture of the acetyl derivative of the simple acid with the diacetyl derivative of its anhydride.

Anal. Subs., 0.1855: CO_2, 0.4337; H_2O, 0.1592. Calcd. for $C_{12}H_{22}O_4$: C, 62.56; H, 9.63. Found: C, 63.85; H, 9.55.

Fifteen grams of this mixture was shaken with 100 cc. of water overnight. An emulsion was formed but the product was easily removed by extraction with 150 cc. of absolute ether. The ether solution was dried with anhydrous magnesium sulfate, filtered and distilled. The product boiled at 168–170° (1 mm.) and was finally recrystallized several times from 100-cc. portions of petroleum ether (b. p. 60–70°). It was thus obtained in shining white plates which melted at 35–36° (corr.). The neutral equivalent and analysis correspond to the theoretical values calculated for the acetyl derivative of w-hydroxydecanoic acid.

Neutral equivalent. Subs., 0.2395: cc. 0.0733 *N* alk., 14.1. Calcd. for $C_{12}H_{22}O_4$: 230.2. Found: 231.

Anal. Subs., 0.2029: CO_2, 0.4670; H_2O, 0.1751. Calcd. for $C_{12}H_{22}O_4$: C, 62.56; H, 9.63. Found: C, 62.77; H, 9.65.

Action of Acetic Anhydride on Poly-esters of w-Hydroxydecanoic Acid.—A 2-g. sample of poly-esters of average molecular weight of 1100 (obtained by melting pure ω-hydroxydecanoic acid in boiling cymene) was introduced into a solution of 1.0 cc. of acetic anhydride in 50 cc. of anhydrous benzene. The resulting solution was refluxed for one hour and then cooled in ice water. The resulting precipitate was filtered and recrystallized once from ethyl acetate. It was observed that this product was more soluble both in benzene and ethyl acetate than the corresponding simple poly-ester. The dried product melted at 68–72" and gave the following values for analysis and neutral equivalent.

Neutral equivalent. Subs., 0.3780: cc. 0.0158 N alk., 15.0; cc. 0.0219 N acid. 1.3. Neut. equiv., 1812.

Anal. Subs., 0.2067: CO_2, 0.5262; H_2O, 0.1948. Calcd. for $CH_3CO_2(CH_2)_9CO$-$[O(CH_2)_9CO]_8$-$O(CH_2)_9CO_2H$: C, 69.48: H, 10.47. Found: C, 69.43; K, 10.54.

This product was then refluxed for two hours with 10% aqueous potassium hydroxide solution. The alkaline solution was cooled and acidified with an excess of phosphoric acid. Upon distillation the distillate was strongly acidic to litmus.

Preparation of the Dimeric Lactone of ω-Hydroxydecanoic Acid.—In a small Claisen distilling flask, 10 g. of the pure potassium salt of ω-hydroxydecanoic acid was covered with acetic anhydride. This mixture was heated just below the boiling point of acetic anhydride for about one hour. The excess acetic anhydride was then removed from the solution on a water pump and the dry potassium salts distilled under a pressure of about 5 mm. A liquid–air trap between the receiving flask and the vacuum pump protected the latter. During the 'distillation the solid salts fused between 350 and 400° (estimated temperature) and distillation occurred between 400–500°. Two products resulted. One of these was an oil which boiled in the neighborhood of 170–190° and was obtained only in small quantities. It was never identified. The second product was a crystalline solid which readily could be recrystallized from acetone and was obtained thus pure as fine, white needles, melting at 95–95.5°. The yield was from 0.3–0.35 g. and was about the same in each of a number of experiments.

A molecular weight determination in benzene agreed with the theoretical value within 4%. *Mol. wt.* Subs., 0.4714; wt. of benzene, 18.61; lowering of f. p. 0 395". Calcd. for $C_{20}H_{36}O_4$, 340. Found: 328.

The values obtained upon analysis for carbon and hydrogen also checked the calculated values. *Anal.* Subs., 0.1881: CO_2, 0.4854; H_2O, 0.1790. Calcd. for $C_{20}H_{36}O_4$: *C*, 70.58; H, 10.67. Found: C, 70.40; H, 10.59.

A 0.2-g. sample of this material was hydrolyzed in 10 cc. of 5% alcohol in potassium hydroxide solution. Water was added and the alcohol removed by distillation. Upon cooling and acidifying with dilute hydrochloric acid, ω-hydroxydecanoic acid precipitated, which was recovered and identified as follows. The aqueous suspension was extracted with several 5-cc. portions of alcohol-free ether. The combined ethereal solutions were washed with water and dried with anhydrous magnesium sulfate. After filtering, the ether was removed under diminished pressure and the product was recrystallized from ethyl acetate. It melted at 75–76° and a mixed melting point with pure ω-hydroxydecanoic acid (m. p. 75–76°) showed absolutely no depression.

A 0.1-g. sample of this product was shaken with 25 cc. of water overnight at a temperature of 20–30°. The product was filtered and recrystallized once from acetone. The melting point remained unchanged at 95–95.5° and a mixed melting point with some of the original material showed no depression.

The dry distillation of the potassium salt of ω-hydroxydecanoic acid led to the formation of water and a high-boiling oil. After separating from the water, the oil was distilled, but no constant boiling fraction was obtained, although the major portion boiled at 170–190°. Attempts were made to hydrolyze this product and to condense it with phenylhydrazine and semicarbazide, but no pure products were isolated.

Summary

1. The intermolecular esterification of w-hydroxydecanoic acid has been studied and found to proceed easily with the formation of mixtures of chain polymers. These mixtures were separated by crystallization into fractions of average molecular weights ranging from 1000 to 9000.

2. These poly-esters were titrated quantitatively with standard alcoholic potash solutions and average molecular weights thus determined. By boiling with excess alcoholic potassium hydroxide, they were converted back to the original acid.

3. A twenty-two-membered dimeric lactone of w-hydroxydecanoic acid was prepared by dry distillation of the product obtained by the action of acetic anhydride on its potassium salt.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE APPARENT RACEMIZATION OF PINENE

BY JAMES B. CONANT AND G. H. CARLSON

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The thermal decomposition of d-pinene was noted by Wallach[1] many years ago in connection with his study of the action of heat on a variety of essential oils. He showed that at 250–270° the final products were dipentene and polymerized material. Very recently Smith[2] has made a quantitative study of the loss of optical activity of pinene at somewhat lower temperatures (185–237°) and concludes that the reaction consists for the most part of a simple racemization. This view he supported by distillation of a sample which had been heated until it had lost about a third of its original optical activity. This evidence did not seem to us conclusive, however, and we decided to determine, if possible, whether the loss of optical activity of pinene was the result of racemization or rearrangement. From a physico-chemical point of view the question is probably of relatively little significance and most of Smith's conclusions are not affected by our final results, which establish that the process he was measuring was in reality a rearrangement and not a racemization. From the standpoint of the organic chemist, however, the point at issue is obviously of importance.

A few experiments convinced us that a definite answer to the problem could not be obtained by fractional distillation. Although there is a 20° difference in the boiling points of pinene (155°) and dipentene (176°), a mixture of equal amounts of the compounds was very incompletely separated by several fractionations through an efficient Widmer column.

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[1] Wallach, *Ann.*, 227, 282 (1885).

[2] Smith, THIS JOURNAL, 49, **43 (1927).**

The incompleteness of the separation was evidenced both by the unsatisfactory boiling points of the high and low fractions and also by the optical activity of what should have been pure inactive dipentene and the low rotation of what should have been pure pinene. We therefore turned to another method of determining the amount of pinene and dipentene in a mixture.

The catalytic hydrogenation of mixtures of pinene and dipentene proved to be a very satisfactory method of determining the proportion of the two constituents. Pinene absorbs one mole of hydrogen, dipentene two; the two compounds are isomeric; therefore the composition of a mixture may be calculated from the amount of hydrogen absorbed by a given weight of material. The method was tested by using both pure compounds and known mixtures; the accuracy of the method is about ±4% of the total hydrogen absorbed. Since difficulty was experienced in obtaining pure dipentene, d-limonene was substituted for it in making the known mixtures (dl-limonene = dipentene). The hydrogenation was carried out in a special constant volume apparatus using Adams' catalyst and glacial acetic acid as a solvent. The details are given in the experimental part of this paper.

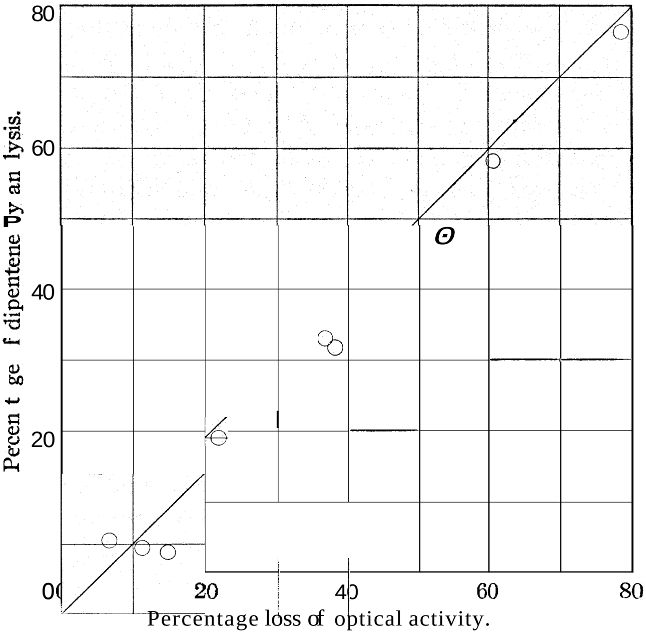

Fig. 1.

Using this method of analysis the amount of dipentene was determined in samples of pinene which had been heated in the gaseous phase at 200 ± 5°

until the optical activity had been diminished. The results are shown graphically in Fig. 1. It is clear that there is a complete parallelism between the amount of dipentene found by the hydrogenation method and the loss of optical activity. There seems no escape from the conclusion that the apparent racemization of pinene is in reality a rearrangement of pinene to dipentene.

Similar results were obtained on heating d-pinene in the liquid phase at 200'. Samples heated until all of the optical activity had been lost (in some cases the rotation became slightly levo) absorbed between 90 and 95% of the amount of hydrogen calculated for pure dipentene. Wallach's original observations were verified by distilling some material which had been heated for 100 hours at 200°. About 30% of polymerized high-boiling material was found and the distillate (b. p. 167–183°) on treatment with bromine yielded crystalline dipentene tetrabromide, though in low yield, which is to be expected in view of the difficulty of obtaining satisfactory amounts of crystalline bromide from pure dipentene.[3]

The Rearrangement of *d*-Pinane.—The saturated dicyclic compound, d-pinane, is much more difficult to rearrange than the corresponding unsaturated compound (d-pinene). For example, heated in the liquid phase for 176 hours at 200°, it lost only 14% of its actvity, whereas the rearrangement of d-pinene at the same temperature was practically complete in fifty hours. It was necessary to heat d-pinane to 285° in order to obtain a rate of rearrangement that was comparable to that of d-pinene at 200°. As in the case of the unsaturated compound, hydrogenation showed that the loss of optical activity is to be attributed to rearrangement and not to racemization. This is clear from Table I, in which the percentage of isomerization was calculated from the amount of hydrogen absorbed, assuming that the product was a monocyclic unsaturated compound, $C_{10}H_{18}$.

As in the case of d-pinene, the rearrangement is accompanied by some polymerization. A sample which had been heated to 285° for fifty hours yielded on distillation a 10% residue of very high-boiling material, The

TABLE I

ISOMERIZATION OF *d*-PINANE IN THE LIQUID PHASE

Time of heating, hours	Temp., °C	Percentage isomerization	
		Calcd from loss of optical activity	Calcd. from hydrogenation
50	200	10.3	7
76	200	12.2	11
176	200	14.1	12
176	200		
and 50	250	35.1	24
52.5	250		
and 50	285	82.4	64

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[3] Wallach, *Ber.*, 40, 603 (1907).

major portion of the distillate boiled at 165–167°, and on catalytic hydrogenation absorbed 65% of the amount of hydrogen calculated for a monocyclic unsaturated compound, $C_{10}H_{18}$. No attempt was made to separate this mixture; undoubtedly a number of isomeric monocyclic compounds are produced and the possibility of some open chain dienes is not excluded.

Experimental

The d-pinene used was purified by fractional distillation over sodium. Two samples were employed in this work which had the following constants: (1) b. p. 156–156.3°, $[\alpha]_D^{23}$ (pure liquid) +43.94°, n_D^{20} 1.4658, d_{20} 0.8600; (2) b. p. 155.3–155.6°, n_D^{20} 1.4560, d_{20} 0.8591, $[\alpha]_{5461}^{23}$ (in acetic acid solution) +65.2°. The d-pinane used was prepared by the catalytic hydrogenation of d-pinene using Adams' catalyst and pressure of 35 lbs. Two samples had the following constants: (I) b p. 167–168.5°, $[\alpha]_{5461}^{23}$ (pure liquid) +26.84°, n_D^{20} 1.4619, d_{20} 0.8579; (2) b. p. 166–166.7°, $[\alpha]_{5461}^{23}$ (pure liquid) +23.71°, n_D^{20} 1.4621, d_{20} 0.8571.

Method of Analysis by Catalytic Hydrogenation.—The catalytic hydrogenation was carried out in a constant volume apparatus so arranged that there was no rubber connection between the reaction vessel and the supply of hydrogen. The reaction vessel, which was a tube about 9 cm. long and had a capacity of about 10 cc., was attached by a ground-glass joint on its upper side and an inverted elbow to a reservoir bulb of about 50-cc. capacity. The bottom of this bulb was constricted and attached by rubber tubing to a leveling bulb. The total volume of the apparatus to a graduation on the constricted bottom of the reservoir was 76.34 cc. About 0.1 g. of material was employed, 2 to 4 mg. of Adams' catalyst and exactly **3** cc. of glacial acetic acid. The apparatus was filled with hydrogen by evacuating and filling three times. The course of the hydrogenation was followed by measuring the pressure difference between the leveling bulb and the constant volume mark. During the hydrogenation a positive pressure of about 3–4 cm. of mercury was maintained. The agitation of the reaction vessel was accomplished by rocking the whole apparatus back and forth about an axis at right angles to the plane of the reaction tube. The pressure was read every half hour until it was constant. The volume of hydrogen absorbed by the catalyst was found to be negligible for one lot of catalyst; for another a correction of ***2*** cc. per ***35*** mg. had to be made.

The following data on the hydrogenation of pure pinene are typical: barometer reading, 757.5; temp., 21.2°; 95.3 mg. of sample; 2.7 mg. of catalyst; pressure difference in mm. of Hg, after 1 hr., 190 mm., after 2 hrs., 189 mm.; cc. of hydrogen found, 17.5; ***cc.*** of hydrogen calculated, 16.95.

In Table II are collected some of the results which demonstrated the applicability of the method for analyzing mixtures of dipentene and *d*-pinene. Since the best samples of dipentene we could obtain absorbed only 80% of the calculated quantity of hydrogen, we substituted *d*-limonene for dipentene.

TABLE II

ESTIMATION OF *d*-PINENE AND *d*-LIMONENE BY CATALYTIC HYDROGENATION

Composition of material taken	Pinene, %	100	0	41	60
	Limonene, %	0	100	59	40
Composition found by catalytic hydrogenation	Pinene, %	103	...	48	53
	Dipentene, %	...	102	**52**	**47**

Isomerization of *d*-Pinene in the Vapor Phase.—The pinene was weighed in a thin-walled bulb which was sealed off and introduced into a bulb of pyrex glass of 300-cc. capacity which was evacuated and sealed. The smaller bulb was then broken and the whole heated in an electric oven at 200 ± 5°. The large bulb, after cooling, was opened and glacial acetic acid added from a weight buret. The rotation of this solution was taken in a decimeter tube using the green mercury line 5461, and the specific rotation calculated and compared with that of the original pinene in glacial acetic acid solution. The analyses of a weighed portion of the solution were then carried out by the catalytic hydrogenation method described above.

In Table III a few typical results are given in full; all of the experiments are summarized in Table IV; the points in Fig. 1 are from Table IV.

TABLE III

TYPICAL DATA OBTAINED IN THE ISOMERIZATION OF PINENE

Temp., 200 ± 5°; time of heating, 1080 min.; $[\alpha]_{5461}$ + 65.2' in acetic acid initially

Expt.	Pinene, mml.	Acetic acid, g.	$[\alpha]_{5461}$	Loss in rotation, %	Sample for analysis, g.	$C_{10}H_{16}$ in sample, mml.	H_2 absorbed. mml.	Dipentene found, %
1	2.978	8.856	$51.0	21.8	3.082	0.9897	1.178	19.1
					3.121	1.005	1.210	21.0
2	3.295	8.743	+40.9	37.7	3.067	1.097	1.515	38.1
					3.111	1.115	1.494	34.0

In calculating $[\alpha]_{5461}$ the density of all of the solutions (which had nearly the same percentage composition) was taken as 1.03.

Since the percentage of dipentene is calculated from the formula

$$\% \text{ dipentene} = \frac{\text{moles } H_2 - \text{moles } C_{10}H_{16}}{\text{moles of } C_{10}H_{16}} \times 100$$

it is evident that the error in determining the amount of hydrogen absorbed is magnified in the calculation of the percentage of dipentene. An error of a few per cent. in the total hydrogen absorbed may make an error of as much as 20% in the percentage of dipentene, if this is small. This effect is evident in Table IV. For this reason duplicate analyses were always carried out.

TABLE IV

SUMMARY OF RESULTS ON THE ISOMERIZATION OF *d*-PINENE IN THE GASEOUS PHASE AT 200 ± 5°

Heating, min.	Loss of rotation, %	Percentage of dipentene by analysis (hyd. method) 1	2	Av.	Heating, min.	Loss of rotation, %	Percentage of dipentene by analysis (hyd. method) 1	2	Av.
720	6.6	11.0	10.0	10.5	2070	36.9	33.9	32.0	33.0
1110	14.9	10.6	7.0	8.8	1080	37.7	38.1	34.0	36.0
1440	11 2	6.74	12.2	9.5	1680	53.7	44.7	50.5	47.6
1080	21.8	19.1	21.0	20.0	2070	60.4	61.7	54.7	58.2
2220	38.2	31.6	31.7	31.7	3030	78.5	77.9	74.7	76.3

Since no attempt was made to hold the temperature constant, the rate of isomerization varied from experiment to experiment. The range of the monomolecular constants was 23.6 X 10^{-5} to 4.2 × 10^{-5} with **a** mean of ten experiments of about 20 X 10^{-5}. Smith gives the value for 198° as 8.6 × 10^{-5} and for 218° as 54 X 10^{-5}. It is thus evident that our process was proceeding at a rate comparable to his and we were studying the same reaction.

Isomerization of *d*-**Pinene** in Liquid Phase.--Samples of d-pinene were sealed in Carius tubes and heated in a gas furnace to 200 * 10°. **A** sample heated for fifty hours showed $[\alpha]_D$ +2.4°, as compared with $[\alpha]_D$ +43.9° initially, percentage loss in rotation, 95; 87.8 mg. of the material with 2 4 mg. of catalyst absorbed 29.3 cc. of hydrogen at 763 mm. and 23°; the calculated amount for pinene is 15.6, the percentage of dipentene was therefore 90. Other samples heated for 100 or 150 hours showed a slight levorotation ($[\alpha]_D$ −0.44 to −0.78'); they absorbed 90 to 95% of the amount of hydrogen corresponding to pure dipentene. 8.8 *g.* of d-pinene which had been heated to 200° for 100 hours yielded 6.7 g. of a distillate, b. p. 167–183.5°; the residue of 1.9 g. was very high boiling. A sample of the distillate absorbed 91% of the amount of hydrogen calculated for dipentene; 2 g. of the same distillate was treated with bromine in ether and alcohol at 0°. On spontaneous evaporation 2.7 g. of crude crystals was left which on recrystallizing from ethyl acetate yielded 1.3 g. of dipentene tetrabromide (m. p. 125°), which was identified by a mixed melting point. Pinene which had been heated for 200 hours at 200° yielded only about 50% of a volatile material (b, p. 172–177°); the residue on distilling in *vacuo* boiled at 180–235° at 2 mm. The fraction which boiled at 172–177° absorbed 92% of the amount of hydrogen calculated for dipentene and yielded the crystalline tetrabromide on brominating.

Isomerization of *d*-**Pinane.**—The pinane was heated in a Carius tube in the same manner as pinene. The material was tested for any unsaturated material before heating, by catalytic hydrogenation in acetic acid in the manner described. No appreciable amount of hydrogen was absorbed. The impurity was therefore less than 1.8%. The results of the isomerization experiments have already been summarized in Table I. The rotation was measured in the pure liquid; the analysis by catalytic hydrogenation was exactly as described for pinene–dipentene mixtures. The amount of unsaturated monocyclic compound, $C_{10}H_{18}$, was taken as equal to the amount of hydrogen absorbed.

A sample of d-pinane (6 g.) which had been heated for fifty hours at 285° yielded 4.8 g. of a distillate, b. p. 165–167°; 0.4 g. of b. p. 170–300°; viscous residue about 0.5 g.; 85.2 mg. of the distillate, b. p. 165–167°, absorbed 9.9 cc. of hydrogen at 767 mm. and 26"; calcd. for $C_{10}H_{18}$ (unsat.), 15.0; 95.6 mg. of the higher fraction absorbed 9.7 cc. of hydrogen at 772 mm. and 26°; calcd. for $C_{10}H_{18}$ (unsat.), 16.7.

Summary

1. The loss of optical activity of d-pinene on heating in the liquid or gaseous phase has been shown to be due to the isomerization to dipentene and not to simple racemization. The presence of dipentene in amounts sufficient to account for the loss of activity has been shown by catalytic hydrogenation.

2. d-Pinane on heating to above 200° in the liquid phase is isomerized with loss of optical activity and the formation of unsaturated hydrocarbons. The process is much slower than in the case of d-pinene.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE KINETICS OF THE POLYMERIZATION OF ACETYLENE[1]

BY ROBERT N. PEASE

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In the course of an investigation of the polymerization of ethylene, some data on the analogous reactions of acetylene were obtained which indicated a relatively simple reaction mechanism. It has seemed worth while to amplify these somewhat and present them for publication, especially in view of the fact that no such study has previously been reported.

It has been known since Berthelot's time that acetylene is readily polymerized on heating, giving a complex of products, many of which are aromatic in character. At the same time, resolution into carbon, hydrogen and methane takes place to a degree which is greater the higher the temperature, as has been shown especially by Bone and Coward.[2] The investigation here reported has had as its object the examination of the manner in which acetylene reacts, rather than the determination of the products of reaction, though some attention has necessarily been given to this point.

The flow method has been used. Acetylene from a tank of this gas was washed with water and dried by calcium chloride. It then passed through a flowmeter into a pyrex reaction tube which was heated in an electric tube-furnace. The off-gas passed through a trap to remove liquid products and thence either to the air or to a small gas-holder, where it could be collected over mercury. The gas was analyzed by absorption in concentrated sulfuric acid to remove higher unsaturated hydrocarbons (correction being made for absorption of acetylene), followed by absorption in dilute bromine water to remove acetylene. In some cases the residue was analyzed for hydrogen and saturated hydrocarbons.

Results

Preliminary experiments revealed that reaction was detectable at 400° on seven minutes' exposure, a white mist appearing in the off-gas accompanied by a rather powerful odor reminiscent of carburetted water-gas. The rate increased rapidly as the temperature was raised and the mist gave place to a brown mobile liquid which collected in the trap.

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[1] This paper contains results of an investigation carried out as part of Project No. 7 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by Mr. John D. Rockefeller. This fund is being administered by the American Petroleum Institute with the cooperation of the Central Petroleum Committee of the National Research Council. Professor Hugh S. Taylor, of Princeton University, is Director of Project No. 7.

[2] Bone and Coward, J. *Chem. Soc.*, **93,** 1197 (1908).

Very little permanent gas was formed until the temperature approached 550°, even though more than half of the acetylene might react. Beyond this point hydrogen and small quantities of methane and ethane appeared. At 600° regular "flashing" began at higher flow rates, though it was possible to carry the reaction to 650° with low flow rates. Experiments were not continued beyond this point. In this high temperature range, finely-divided carbon was carried out of the tube.

Liquid Products,—Some attention was given to the more volatile liquid products, with the special purpose of determining whether benzene formation preponderated. The liquid was placed in a small flask to which was sealed a collecting tube and a stopcock. The system was evacuated after cooling the liquid to −79°. The flask was then held at 25° while the collecting tube was at −79°. Distillation took place rather rapidly, and in different experiments from one-third to three-fourths of the liquid came over. The distillate had in all cases a density close to 0.850 (benzene 0.878, dipropargyl 0.805), which was indicative of aromatic character. It did not freeze sharply but was in general completely solid at −10 to −20°. This material was considerably polymerized (or carbonized) by concentrated sulfuric acid but gave a residue which after distillation was solid at −3°, and which gave nitrobenzene on nitration. The original distillate gave no test with ammoniacal cuprous chloride solution, indicating the absence of compounds with terminal CH groups (such as dipropargyl). The indication is that benzene formation does occur but that it does not predominate under the conditions of these experiments.

About a half of the residue from the above distillation distilled over up to 300°, leaving a pitch. Nothing further was done with this.

Reaction Kinetics.—Preliminary experiments revealed that the reaction rate varied with concentration and time, approximately as would be expected for a bimolecular reaction. Thus, for example, at 550° and 1 atm. total pressure, 32% of the acetylene reacted in twenty-five seconds when the pure gas was admitted, and 18% when the acetylene was diluted with its own volume of nitrogen. If the reaction is bimolecular and the conversion is low (lower than the above figures), dilution with nitrogen should have cut the yield in half. It is obvious that this state of affairs is approached, and that we are dealing with a process which is initiated by a change involving two molecules.

The question arises as to whether the reaction is homogeneous, or takes place on the walls. To answer this, experiments were carried out with a reaction tube packed with broken pyrex glass (4–20 mesh). Under these conditions the yield was materially decreased. Thus, at 550° and 1 atm., only 17% reacted in twenty-five seconds when the gas was pure acetylene, as compared to 32% in the empty tube. The conversion is nearly halved. The indication is thus not of a positive but rather of a negative catalytic action of the walls. This is doubtless bound up with the exothermicity of the reactions which are taking place. The condensation of three molecules of acetylene to benzene would liberate 149,200 cals. per mole of benzene, for example. The wall material may be assumed to act to maintain the temperature, or to deactivate excited product materials.

The results of the rate measurements are conveniently expressed in terms of a bimolecular reaction constant. The calculation of such constants cannot be put on an altogether satisfactory basis, however. These reactions are carried out at constant pressure and involve a volume decrease. Hence the time of heating depends upon the amount of reaction, since the resulting volume contraction progressively decreases the linear flow rate within the reaction tube. Further, the true volume contraction at all points within the reaction tube is unknown because of the complexity of the reactions, and uncertainty as to whether the polymerization is entirely completed within the reaction tube. Under the circumstances a precise analysis of the results is not possible. The best that can be done is to assume some average value for the volume change and calculate on this basis. Considering the results of the distillation analyses, it has seemed most reasonable to set this at 4 to 1, which amounts to assuming that the average composition of the product is $(C_2H_2)_4$.

The rate constants are calculated in the following way. We assume that the primary reaction, which is the slow rate-determining process, is $2C_2H_2 \longrightarrow (C_2H_2)_2$. This is followed by a series of rapid reactions such as $(C_2H_2)_2 + C_2H_2 \longrightarrow (C_2H_2)_3$, etc., which lead to the final product whose composition is on the average $(C_2H_2)_4$. Let v_0 be a volume of acetylene and v_N a volume of nitrogen admitted to the reaction tube at a rate of S_0 cc./second. These and all volumes are for the moment considered as measured at the temperature and pressure of the reaction tube. At some later time a volume, $v_0 - v$, of acetylene has reacted to give $1/4(v_0 - v)$ of product. The total volume of gas at this time is

$$V_g = v + v_N + {}^1/_4(v_0 - v) = {}^1/_4v_0 + v_n + {}^3/_4v$$

The corresponding flow rate is

$$S = S_0 \frac{V_g}{v_0 + v_N}$$

Suppose the gas is passing through a cylindrical reaction tube of length, l, and cross section πr^2. At any point, l', along the tube, the linear flow rate is

$$\frac{dl}{dt} = \frac{S}{\pi r^2} = \frac{S_0}{\pi r^2(v_0 + v_N)} \times V_g$$

Consider a section of the tube at l' equal to ar^{2}dl. Any element of gas volume is in this section for a time dt. During this time some reaction takes place. If the action is bimolecular, we may write for its rate

$$-\frac{1}{v}\frac{\mathrm{d}v}{\mathrm{d}t} = k\frac{v}{V_g} \times \frac{p}{760}$$

where k is the fractional conversion per second when the acetylene is at a pressure of 1 atm. Eliminating dt from these equations, we obtain

$$\frac{\pi r^2(v_0 + v_N)}{s_0 V_g}\,\mathrm{d}l = \frac{V_g \cdot 760}{kv^2 \cdot p}\,\mathrm{d}v$$

Integrating and solving for k, we obtain

$$k = \frac{760\ S_0}{p(v_0 + v_N)V_r}\left[{}^9/_{16}\,(v_0 - v) + {}^6/_4({}^1/_4 v_0 + v_N)\ln\frac{v_0}{v} + ({}^1/_4 v_0 + v_N)^2\frac{v_0 - v}{v - v_0}\right]$$

Here $V_r = \int_0^l \pi r^2 \mathrm{d}l$ = volume of the reaction tube.

The gas volumes are supposed to have been measured at the temperature and pressure of the tube. An examination of the above equation indicates, however, that any other basis of comparison is equally good, provided only that the actual tube volume be corrected to correspond, for we may as well think of the tube shrinking as of the gases expanding. Since the gas volumes were all corrected to 25° and 1 atm., the tube volume has been calculated to these conditions and is so recorded.

Data on experiments between 400 and 650° are given in Table I.

TABLE I

RESULTS

Temp., °C.	Tube[a]	Eff. tube vol., cc.	Inflow rate, cc./sec.	N_2, cc.	C_2H_2, cc. In	Out	Reacted	Found, cc. H_2	CH_4	C_2H_6	C_nH_m[b]	Atm. press., mm.	k_2
400	A	285	0.671	2	98	97	1	←	1	→	1	768	.....
450	A	265	.667	2	98	88	10		0		2	766	0.00018
	A	265	.334	2	98	75	23		6		3	766	.00022
	A	256	.164	2	96	65	31		2		2	742	.00016
	A	265	.669	51	49	46	3		0		2	767	.....
475	A	252	.665	2	97	72	25		3		4	754	.00050
	A	254	.336	2	99	57	42		4		3	760	.00043
	A	254	.168	2	99	39	60		5		2	761	.00034
	A	254	.670	52	49	43	6		0		2	760	.....
500	A	248	.672	2	99	48	51		4		3	769	.0011
	A	248	.674	52	50	34	16		0		3	768	.0015
525	B	97.2	.662	2	97	44	53		3		3	755	.0030
	B	97.5	.663	51	49	31	18		1		4	755	.0045
550	C	17.1	.662	2	97	66	31	←	2	→	3	760	.0092
	B	94.0	.651	2	96	22	74	4	1	1	2	753	.0054
	C	17.0	.669	53	49	40	9	←	0	→	3	759	.011
	B	94.3	.654	51	48	23	25	3	0	1	3	755	.0083
	D	8.41	.685	2	101	95	6	←	2	→	3	767	.....
	D	8.39	.340	2	101	84	17	←	1	→	4	765	.0049
575	C	16.4	1.32	2	97	61	36	←	2	→	3	752	.023
	C	16.4	0.657	2	97	41	56	2	0	1	3	749	.019
	B	91.9	.678	2	100	12	88	7	5	0	2	758	.....
	C	16.4	.659	50	48	33	15	←	0	→	2	750	.021

TABLE I (*Concluded*)

Temp., °C.	Tube[a]	ER. tube vol., cc.	Inflow rate, cc./sec.	N_2, cc.	C_2H_2, cc.			Found, cc.				Atm. press., mm.	k_2
					In	Out	Re-acted	H_2	CH_4	C_2H_6	C_nH_m[b]		
	B	91.7	0.673	52	50	16	34	3	0	1	3	757	0.015
	D	8.74	.672	2	101	83	18	←	1	→	3	767	.0099
	D	8.70	.340	2	100	64	36	←	1	→	3	765	.011
600	C	15.7	.648	2	95	21	74	4	2	0	3	740	.033
	B	89.3	.662	2	97	6	91	9	8	1	2	759	.....
600	C	15.6	.643	49	47	24	23	3	0	1	4	734	.045
	B	89.2	.664	51	49	8	41	5	1	1	3	758	.....
	D	7.84	1.35	2	99	80	19	←	1	→	4	759	.024
	D	7.85	0.673	2	99	55	44		2		3	760	.030
	D	7.74	1.338	2	100	29	71		4		2	760	.029
	D	7.75	0.675	52	50	40	10	←	1	→	3	760	.025
650	C	14.5	.680	2	98	8	90	9	5	3	1	757	.....

[a] The dimensions of the reaction tube were as follows:

Tube	A	B	C	D
Diameter, cm.	4.3	4	2.5	3
Length, cm.	40	22	12	10
Volume, cc.	637	262.4	47.2	23.0 packed

[b] "C_nH_m" refers to the higher volatile hydrocarbons absorbed in concd. sulfuric acid.

Conclusions

The data show clearly that polymerization is the only reaction of importance up to 600°, though secondary or less important primary reactions do begin to yield hydrogen and methane at the higher temperatures. The polymerization produces a complex of products, as has already been pointed out, and there is no evidence from these results that any one product predominates under any particular set of conditions. Especially, there is no evidence of a quantitative yield of the first product of polymerization of two molecules of acetylene. This might be expected to show under "C_nH_m," which represents absorption in concd. sulfuric acid.

Although the kinetic studies are not conclusive, the indication is that the rate-determining process is the primary reaction involving two molecules of acetylene. The reaction is shown to be homogeneous by the fact that the rate is not increased by a glass packing, but is actually decreased. This decrease is undoubtedly bound up with the exothermic nature of the reactions taking place.

Summary

The polymerization of acetylene has been studied by the flow method. Results indicate that the polymerization is a homogeneous, bimolecular reaction which is partially suppressed by use of a glass packing. The polymerization is the only reaction of importance between 400 and 600°. It yields a complex of products of a wide range of volatility. Benzene

is present along with other volatile hydrocarbons subject to attack by concd. sulfuric acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

SOME REARRANGEMENT REACTIONS OF ALPHA-NAPHTHYLMETHYLMAGNESIUM CHLORIDE

BY HENRY GILMAN AND JAMES E. KIRBY

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Introduction

In continuation of investigations[1] concerned with so-called rearrangements of some organomagnesium halides, a study has been made of the reactions of a-naphthylmethylmagnesium chloride (α-$C_{10}H_7CH_2MgCl$). It is known that some RMgX compounds (in particular, benzylmagnesium chloride and triphenylmethylmagnesium chloride) react both normally and abnormally with some reagents, especially with aldehydes.[2] We wished to ascertain whether such abnormal reactions were characteristic of organomagnesium halides with the grouping $>C{=}\overset{|}{C}{-}CH_2MgX$. The results of the present study show that a-naphthylmethylmagnesium chloride does behave abnormally with some compounds that give rise to rearrangement products with a type like benzylmagnesium chloride. Accordingly, mechanisms to be offered[2] for such rearrangements must include a-naphthylmethylmagnesium chloride.

The preparation of a-naphthylmethylmagnesium chloride by earlier investigators has been attended with more than ordinary difficulties. Weitzenbock and Lieb[3] had no success in the synthesis of ethyl α-naphthylacetate from a-naphthylmethylmagnesium chloride and ethyl chlorocarbonate. They probably did not have any of the desired Grignard reagent in hand. When they treated a-naphthylmethyl chloride (prepared by the direct chlorination of α-methylnaphthalene)[4] with magnesium they had difficulty in getting the magnesium to react, and after treating their reaction mixture with ethyl chlorocarbonate, the only product they isolated was di-a-naphthylethane formed as a result of a coupling reaction.[5] Then Mayer and Sieglitz[6] found that magnesium was used up to only a

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[1] Gilman and Harris, THIS JOURNAL, **49,** 1825 (1927).

[2] A later report will describe many other reagents that react abnormally with such types.

[3] Weitzenbock and Lieb, *Monatsh.*, **33,** 554 (1912).

[4] Scherler, ***Ber.*, 24,** 3930 (1891); Wislicenus and Wren, *ibid.*, **38,** 506 (1905).

[5] Gilman and Fothergill, THIS JOURNAL, 50, 3334 (1928).

[6] Mayer and Sieglitz, ***Ber.*,** 55, 1835 (1922). They prepared their bromide by the direct bromination of a-methylnaphthalene.

slight extent in its reaction with a-naphthylmethyl bromide, and they also obtained only the coupling product (di-α-naphthylethane) in a reaction with acetaldehyde. More recently, Conant, Small and Sloan[7] had better success with their chloride prepared by the method of v. Braun and Moldaenke.[8] However, their chloride reacted slowly with magnesium and the reaction was about complete at the end of three hours; their yield of crude a-naphthylmethylxanthenol from xanthone was about 15%.

Our chloride, prepared from a-naphthylcarbinol and thionyl chloride, reacted with comparative ease with ordinary magnesium turnings to give quite satisfactory yields[g] of several products. Abnormal reactions were observed with ethyl chlorocarbonate and formaldehyde, the products having the carboxyethyl and carbinol groups, respectively, in the β- and not in the a-position. Normal products were obtained with carbon dioxide, dimethyl sulfate and phenyl isocyanate.

One reaction was carried out between the relatively inaccessible and expensive β-naphthylmethylmagnesium bromide and carbon dioxide, and the expected β-naphthylacetic acid was obtained.

Experimental Part

Preparation of a-Naphthylmethyl Chloride.—First, α-naphthylcarbinol was prepared in 50–53% yield in accordance with the method of Ziegler[10] by the action of gaseous formaldehyde on a-naphthylmagnesium bromide. Then, to 25 g. (0.15 mole) of the carbinol dissolved in 100 cc. of dry toluene was added 25 g. of thionyl chloride in small quantities. A reaction set in at once and after the spontaneous reaction ended the solution was refluxed gently until evolution of gases ceased. This required about three hours. The toluene and thionyl chloride were removed under reduced pressure and fractional distillation of the residue gave 23.2 g. or a 79% yield of the chloride boiling at 135–139° (6 mm.).

Preparation of the Grignard Reagent.—In a first experiment we used a-naphthylmethyl chloride prepared by the direct chlorination of α-methylnaphthalene.[4] Although we obtained the Grignard reagent from this chloride, the reaction was unsatisfactory. In all subsequent experiments we used the chloride prepared from the corresponding carbinol With this chloride reaction set in as readily as with bromobenzene and magnesium when the usual small crystal of iodine was used as a catalyst.

In some preliminary experiments the reagent was prepared in a test-tube in connection with the color test of Gilman and Schulze.[11] It was observed that once the

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[7] Conant, Small and Sloan, THIS JOURNAL, **48**, 1743 (1920).

[8] V. Braun and Moldaenke, *Ber.*, 56, 2165 (1923).

[9] No study was made of optimal conditions ior the preparation of the a-naphthylmethylmagnesium chloride. It is highly probable, however, that yields of about 90% or more can be obtained by following the directions of Gilman and McGlumphy, Bull. *soc. chim.*, **43**, 1322 (1928), for the preparation of allylmagnesium bromide. Judging by the yields of some of the products obtained from a-naphthylmagnesium chloride it is fair to state that this Grignard reagent was obtained in the present study in yields of at least 80%. See Gilman and St. John, *Rec. trav. chim.*, **48**, 593 (1929).

[10] Ziegler, *Ber.*, **54**, 737 (1921).

[11] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925); *Bull. soc. chim.*, **41**, 1479 (1927).

reaction started it continued in the presence of the Michler's ketone to give a pronounced characteristic color test on subsequent hydrolysis. Of course the same test was obtained in another test-tube experiment when the ketone was added after the reaction between the chloride and magnesium was complete.

In the subsequent reactions, 10 g. (0.057 mole) of the a-naphthylmethyl chloride in 50 cc. of ether was added slowly to 1.38 g. (0.057 atom) of magnesium turnings covered with 85 cc. of ether.[12] The RMgCl solution was of a yellowish-green color.

Carbon Dioxide.—a-Naphthylacetic acid was prepared in the customary manner[13] from carbon dioxide. A negative color test[11] was obtained at the end of twenty minutes. The yield of acid from 0,057 mole of chloride was 59.4%.[9] It was characterized both by its melting point and the melting point of α-naphthylacetamide[14] prepared from it.

Dimethyl Sulfate,—The reaction between the Grignard reagent (0.057 mole of chloride) and dimethyl sulfate was carried out in accordance with the general directions of Gilman and co-workers.[15] The yield of a-ethylnaphthalene was 55.1%. It distilled at 247–249° (742 mm.) and was identified as the picrate, which melted at 98–99°. The melting point of the picrate as reported by Carnelutti[16] is 98°.

Phenyl Isocyanate.—A vigorous reaction took place when 10 g. (0.08 mole) of phenyl isocyanate in ether was added slowly to the Grignard reagent prepared from 17.6 g. (0.1 mole) of a-naphthylmethyl chloride. After working up the reaction product in a customary manner,[17] 9.3 g. or a 36% yield of α-naphthyl acetanilide was obtained. The compound melted at 155° when crystallized from alcohol and its identity was confirmed by a mixed melting point determination with the anilide prepared from α-naphthylacetyl chloride[18] and aniline.

In a preliminary experiment it was noticed that phenyl isocyanate stopped a reaction between a-naphthylmethyl chloride and magnesium. This reaction could not be induced to start again either by warming or by the addition of iodine. A similar case of negative catalysis with phenyl isocyanate was noted earlier by Gilman and Kirby[19] with benzohydrylmagnesium chloride $(C_6H_5)_2CHMgCl$. In another experiment a small quantity of an as yet unidentified solid melting at 136–137" was obtained. This may be a rearrangement product.

Ethyl Chlorocarbonate.—The Grignard reagent prepared from 0.095 mole of the chloride was rapidly decanted from unused magnesium into a separatory funnel, and then added slowly to 43 g. (0.4 mole) of ethyl chlorocarbonate in ether. On working up the reaction products in a customary manner, subsequent to hydrolysis by iced dilute hydrochloric acid, a 41% yield of ester distilling at 145–150° (3 mm.) was obtained. The ester was hydrolyzed by heating with alcoholic potash and the acid obtained from the hydrolysis melted at 174°. It may be crystallized from either hot water or benzene.

The neutralization equivalent (184.8, whereas the calculated value for $C_{12}H_{10}O_2$ is 186) showed it to be isomeric with α-naphthylacetic acid. It was definitely shown to be a-methyl-p-naphthoic acid by a mixed melting point determination with an

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[12] For general directions on the preparation of Grignard reagents see Gilman, Zoellner and Dickey, THIS JOURNAL, **51,** 1576, 1583 (1929).

[13] Gilman and Parker, *ibid.,* **46,** 2816 (1924).

[14] Boessneck, *Ber.,* **16,** 641 (1883).

[15] A recent leading reference is Gilman and Heck, THIS JOURNAL, **50,** 2223 (1928).

[16] Carnelutti, *Ber.,* **13,** 1671 (1880).

[17] Gilman and Furry, THIS JOURNAL, **50,** 1214 (1928).

[18] Prepared from a-naphthylacetic acid and thionyl chloride by heating in a benzene solution. The acid chloride was not isolated.

[19] Gilman and Kirby, THIS JOURNAL, **48,** 1734 (1926).

authentic specimen of the acid kindly provided by Professor v. Auwers.[20] This rearrangement product is remindful of a like rearrangement of benzylmagnesium chloride2 which with ethyl chlorocarbonate gave both ethyl o-toluate and ethyl phenylacetate. The ester described above is undoubtedly chiefly ethyl a-methyl-p-naphthoate.

The anilide of α-methyl-β-naphthoic acid was prepared after the method[1]*used for the preparation of the anilide of a-naphthylacetic acid and melted at 217–218° after crystallization from alcohol.

No definite products were obtained in the attempts to oxidize a-methyl-p-naphthoic acid by alkaline permanganate and by chromic acid in acetic acid. Mayer and Schnecko[21] also had no success in their attempts to oxidize the same acid to α,β-dicarboxynaphthalene.

Formaldehyde.--The reaction between gaseous formaldehyde and the Grignard reagent prepared from **0.1** mole of the chloride gave 6.4% of the coupling product (di-a-naphtbylethane), an as yet unidentified small fraction distilling between 100–130° **(6** mm.) and **2.6** g. of a yellow oil distilling at 167–170° **(6** mm.) and melting at 121° when crystallized from benzene. It showed reactions of an active hydrogen compound and its phenylurethan (prepared from phenyl isocyanate in benzene) melted at 125°. No definite product was obtained in the attempted oxidation of the carbinol by means of alkaline permanganate to the corresponding acid. In this connection it is interesting to note that Ziegler and Tiemann[22] were unsuccessful in their attempted oxidation of the isomeric β-methyl-α-naphthylcarbinol to the corresponding aldehyde. They used chromic acid; a part of their carbinol was completely oxidized and the remainder was unchanged. These difficulties in oxidation may be due to steric influences. Undoubtedly the carbinol is α-methyl-β-naphthylcarbinol formed as **a** result of a rearrangement reaction that has been confirmed by several with benzylmagnesium chloride and formaldehyde. None of the normal and known reaction product, a-naphthylethyl alcohol, has as yet been isolated.

The Reaction between β-Naphthylmethylmagnesium Bromide and Carbon Dioxide.—The reaction between β-naphthylmethyl bromide and magnesium in ether started easily with the aid of a crystal of iodine. The Grignard reagent was carbonated in the customary manner[13] and the β-naphthylacetic acid obtained after crystallization from benzene melted at 138°. Its identity was confirmed by a mixed melting point determination with the acid prepared according to Blank[23] by the hydrolysis of β-naphthylacetonitrile.

Summary

It has been shown that α-naphthylmethylmagnesium chloride can be readily prepared in satisfactory yields and that it reacts normally with carbon dioxide, dimethyl sulfate and phenyl isocyanate, but abnormally with ethyl chlorocarbonate and formaldehyde. The rearrangement reactions of this organornagnesium chloride can be correlated with like reactions shown by compounds with the $—CH{=}CHCH_2MgX$ grouping.

AMES, IOWA

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[20] v. Auwers and Moller, *J. prakt. Chem.,* **109, 124 (1925).**

[21] Mayer and Schnecko, *Ber.,* 56, **1408 (1923).**

[22] Ziegler and Tiemann, *ibid.,* 55, **3406 (1922).**

[23] Blank, *ibid.,* 29, **2372 (1896).**

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

THE ACTION OF AROMATIC GRIGNARD REAGENTS ON ARYLARSINE OXIDES[1]

BY F. F. BLICKE AND F. D. SMITH[2]

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The preparation of several tetra-arylarsyl oxides from arsenic trioxide and arylmagnesium halides has been described recently and a reaction mechanism to account for their formation has been suggested.[3]

A second method for the preparation of tetra-arylarsyl oxides, by means of which simple as well as mixed oxides of the type RR'As—O—AsR'R can be obtained, is the subject of this paper.

Diphenyl, di-p-tolyl, di-p-anisyl and di-a-naphthyl mercury were prepared by the interaction of arylmagnesium halides and mercuric chloride. $RMgX + HgCl_2 \longrightarrow RHgX + ClMgX$; $RHgX + RMgX \longrightarrow RHgR + MgX_2$. Hitherto only diphenylmercury has been obtained by this method.[4]

The diarylmercury compounds were heated with arsenic trichloride with the formation of aryldichloro-arsines which, upon hydrolysis, yielded arylarsine oxides.

$$RHgR + AsCl_3 \longrightarrow RAsCl_2 + ClHgR$$
$$ClHgR + AsCl_3 \longrightarrow RAsCl_2 + HgCl_2$$
$$RAsCl_2 + 2NaOH \longrightarrow RAsO + 2NaCl + H_2O$$

In those instances in which it is impractical to prepare the mercury diaryls, the oxides can be obtained by reduction of the corresponding diarylarsinic acids.

The arylarsine oxides, when allowed to react with an aromatic Grignard reagent, were converted into tetra-arylarsyl oxides, as follows

$$2RAs{=}O + 2\,RMgX \longrightarrow 2RRAs(OMgX)$$
$$2RRAs(OMgX) + 2H_2O \longrightarrow RRAs{-}O{-}AsRR$$
$$2RAs{=}O + 2R'MgX \longrightarrow 2RR'As(OMgX)$$
$$2RR'As(OMgX) + 2H_2O \longrightarrow RR'As{-}O{-}AsR'R$$

The simple tetra-arylarsyl oxides were obtained directly from the reaction mixture in crystalline form. The mixed oxides, however, could be isolated only in the form of oils which would not crystallize. These products were treated with chlorine,[5] the crystalline tetrachlorides hydrolyzed to the arsinic acids, the latter reduced and the reduction products

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[1] This paper represents the second part of a dissertation submitted to the Graduate School by Mr. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Parke, Davis and Company Fellow, 1927–1929.

[3] Blicke and Smith, THIS JOURNAL, 51,1558 (1929).

[4] Pfeiffer and Truskier, *Ber.*, 37, 1127 (1904).

[5] In some instances the tetra-arylarsyl oxides were oxidized directly to the diarylarsinic acids by means of warm alkaline hydrogen peroxide.

isolated in the form of the diarylarsyl halides. The latter when hydrolyzed yielded the pure tetra-arylarsyl oxides

$$\mathrm{RR'As{-}O{-}AsRR'} \longrightarrow \mathrm{RR'As(Cl_2){-}O{-}As(Cl_2)R'R} \longrightarrow \mathrm{2RR'As(O)OH}$$
$$\mathrm{2RR'AsCl} \longrightarrow \mathrm{RR'As{-}O{-}AsR'R}$$

Experimental Part

Preparation of Mercury Diaryls

General Procedure.—The Grignard reagent was prepared in a liter, three-necked flask from **0.4** mole of the aryl halide, **0.4** of an atomic equivalent of magnesium and **200** cc. of ether. A mechanical stirrer was introduced and the arylmagnesium halide diluted with **100** cc. of dry benzene. Forty-eight g. **(0.18** mole) of dry mercuric chloride was added, cautiously, in four portions during the course of an hour with rapid stirring; the stirring was continued for eight hours. The reaction mixture, which consisted of the mercury diaryl and the arylmercuric halide, was treated with ice and a small amount of hydrochloric acid. In the case of mercury diphenyl, the ether-benzene layer was decanted, filtered and dried with fused sodium sulfate. The solvent was removed and the residue washed with petroleum ether (40–60°). In the preparation of mercury ditolyl only a small amount of the substance is present in the ether-benzene layer and in the case of mercury dianisyl and mercury dinaphthyl practically all of the material is found in the reaction mixture as a precipitate. In the latter instance the dry mixture of the mercury diaryl and the arylmercuric halide was placed in a Soxhlet apparatus and the diaryl mercury extracted with benzene.

TABLE I

MERCURY DIARYLS

	Diphenyl[a]	**Di-*p*-tolyl**[b]	**Di-*p*-anisyl**[b]	**Di-a-naphthyl**[c]
M. p., °C.	**121**	**235–238**	**198–200**	**240–243**
Yield, %	**75**	**70**	**62**	**90**

[a] Pfeiffer and Truskier, ref. 4, obtained a **42%** yield; m. p. 120°. [b] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, 1921. [c] Matsumiya, Mem. *Coll. Sci. Kyoto Imp. Univ.*, *8*, **394** (1925), obtained this compound from α-naphthylmagnesium bromide and α-naphthyl mercuric chloride in **69%** yield.

Preparation of Arylarsine Oxides

General Procedures (a).—The mercury diaryl was heated with one and one-half times the theoretical amount of freshly distilled arsenic trichloride for three hours at 130–140°. The reaction mixture was extracted with benzene and filtered. After removal of most of the benzene on a steam-bath, the mixture was distilled under diminished pressure in an atmosphere of nitrogen until the excess arsenic trichloride had been removed. The crude aryldichloro-arsine was added to a warm **10%** solution of sodium hydroxide with rapid stirring; sufficient alkali should be used to dissolve all of the arylarsine oxide formed. The solution was filtered from mercury compounds through a Jena filter. The alkaline filtrate was neutralized, the precipitate washed by decantation and then filtered.

The oxides, with the exception of the naphthyl compound, were dissolved in hot benzene and an equal volume of absolute ether added to the cold benzene solution. The oxides precipitated slowly. The naphthylarsine oxide was obtained in a pure state in the following manner: the crude oxide was suspended in benzene, treated with dry hydrogen chloride and the solution of naphthyldichloro-arsine heated until the solvent was removed. A small amount of petroleum ether **(40–60°)** was added to the oily residue. The latter became crystalline and the material was then recrystallized from petroleum ether; m. p. 70–72°.[6] Upon hydrolysis of the dichloride there was obtained pure naphthylarsine oxide.

(b) Sulfur dioxide was passed into a mixture prepared from one part of the arylarsinic acid,[7] five parts of methyl alcohol, two parts of concd. hydrochloric acid and about 0.1 g. of potassium iodide dissolved in a small amount of water. The greater part of the aryldichloro-arsine formed precipitated as an oil. Water was added to precipitate the chloride completely and after decantation of the aqueous layer the oil was washed thoroughly with water. The oily chloride was treated with warm 10% sodium hydroxide until a clear solution was obtained. The latter was neutralized, whereupon the arylarsine oxide precipitated.

TABLE X

ARYLARSINE OXIDES

	Phenyl	*p*-Tolyl	*p*-Anisyl	α-Naphthyl
M. p., °C.	144–146[a]	188–190[b]	114–116[c]	245[d]
Yield (method a),[e] %	60	.....	.....	60
Yield (method b),[f] %	80	87	90	..

[a] Michaelis, Ber., 10, 623 (1877), recorded the melting point as 119–120°. Gryszkiewicz-Trochimowski, Mateyak and Zablotscki, Bull. soc. chim., [4] 41, 1327 (1927), state that the substance melts at 129–130° when prepared by hydrolysis of phenyldicyano-arsine. [b] La Coste and Michaelis, Ann., 201, 257 (1880), found the melting point to be 156°. Tolyldichloro-arsine, from which this oxide was prepared by hydrolysis, was analyzed. Calcd. for $C_7H_7AsCl_2$: Cl, 29.95. Found: 29.87, 29.65. [c] Michaelis and Weitz, Ber., 20, 51 (1887), described this substance as a crystalline crust but recorded no melting point. When this compound is recrystallized from a mixture of benzene and ether, it melts at 93–95° and seems to lose solvent of crystallization. After it has been heated it melts at 114–116°. The latter melting point was obtained when the compound was recrystallized from a mixture of chloroform and ether. [d] If the oxide is dissolved in alkali, precipitated with an acid and then air dried it melts at 245°. After recrystallization from tetralin the melting point was 206–210°. When the compound obtained from tetralin was heated with benzene the melting point was 185–190°. Solvent of crystallization can be seen to escape from the melting-point tube when the latter is heated. [e] The yield is based on the diaryl mercury compound. [f] The yield is based on the arylarsinic acid which had been recrystallized from water.

Interaction of Arylmagnesium Halides and Arylarsine Oxides

General Procedure.—Three hundredths of a mole of the arylarsine oxide was dissolved in 100 cc. of dry benzene, the solution cooled with ice and stirred rapidly. Forty-five hundredths of a mole of the Grignard reagent was then added. After one-half hour the ice-bath was removed and the mixture was stirred for four hours longer. After twelve hours the reaction mixture was decomposed with ice and a small amount of acetic acid, the ether–benzene layer separated, washed with 10% sodium hydroxide and then dried over fused sodium sulfate. The solvents were removed and the oily residue, which could not be obtained in crystalline form in the case of the mixed tetra-arylarsyl oxides, RR′As—O—AsR′R, was dissolved in absolute ether and the solution saturated with chlorine. The tetrachloro derivative of the tetra-arylarsyl oxide precipitated to some extent in the form of an oil which soon became crystalline. The solvent was removed from the mixture and the residue treated with 5% sodium hydroxide

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[6] Gryszkiewicz-Trochimowski, Mateyak and Zablotscki, Bull. *soc. chim.*, *[4]* 41, 1328 (1927), record the melting point as 69.5–70°.

[7] The arylarsinic acids were all prepared according to the method of Schmidt, Ann., 421, 169 (1920).

solution to convert the tetrachloride into the arsinic acid. The alkaline solution of the latter substance was extracted with ether to remove by-products, the solution heated on a steam-bath to remove dissolved ether and then neutralized, whereupon the arsinic acid precipitated in the form of a gum; after some time the latter became solid. The crude arsinic acid was boiled with acetone, the solution cooled and then filtered. This process was repeated several times. The arsinic acid dissolves in the acetone only to a slight extent but the by-products in the crude acid are much more soluble. Phenylbiphenylarsinic acid can be recrystallized from alcohol.

The diarylarsinic acid was then converted into the diarylarsyl chloride by the action of sulfur dioxide and hydrochloric acid in the same manner as described above under general procedure (b). The diarylarsyl chloride precipitated immediately in some cases as an oil, in other instances as a solid. The chloride was then heated with alcoholic sodium hydroxide, whereby it was converted into the tetra-arylarsyl oxide.

TABLE III

DIARYLARSINIC ACIDS[a]

	M. p., °C.	Formula	Arsenic analyses[c] Calcd.	Found
Phenyl-*p*-tolyl	148–150[b]	$C_{13}H_{13}AsO_2$	27.17	27.65
Phenyl-*p*-anisyl	167–169	$C_{13}H_{13}AsO_3$	25.68	26.08
Phenyl-a-naphthyl	175–176	$C_{16}H_{13}AsO_2$	24.03	24.87
Phenylbiphenyl	218–220	$C_{18}H_{15}AsO_2$	2220	22.10
p-Anisylbiphenyl	228–231	$C_{19}H_{17}AsO_3$	20.38	20.59

[a] All of the diarylarsinic acids are practically insoluble in hot acetone, soluble in a mixture of alcohol and hydrochloric acid, soluble in hot benzene and only slightly soluble in hot water. [b] Michaelis, **Ann.**, 321, **157** (1902), recorded the melting point as 158–160". [c] Ewin, *J. Chem. Soc.*, **109**, **1356** (**1916**).

TABLE IV

DIARYLARSYL CHLORIDES

	M. p., °C.	Formula	Chlorine analyses (Volhard) Calcd.	Found
Phenyl-*p*-tolyl[a]	Oil	$C_{13}H_{12}AsCl$	12.73	12.67
Phenyl-*p*-anisyl	Oil	$C_{13}H_{12}OAsCl$	12.04	12.26
Phenyl-a-naphthyl	Oil	$C_{16}H_{12}AsCl$	11.27	11.12
Phenylbiphenyl	83–85°	$C_{18}H_{14}AsCl$	10.41	10.31
p-Anisylbiphenyl	Oil	$C_{19}H_{16}OAsCl$	9.57	10.01

[a] Michaelis, Table III, footnote b, states that this substance is an oil.

TABLE V

TETRA-ARYLARSYL OXIDES

	Reagents for the preparation Oxide	Mg compound	M. p., °C.
Diphenyl-di-*p*-tolyl[a]	Phenylarsine	Phenyl-Mg-bromide	7.577
Diphenyl-di-*p*-anisyl	Phenylarsine	Anisyl-Mg-iodide	Oil
Diphenyl-di-a-naphthyl	Phenylarsine	Naphthyl-Mg-bromide	Oil
Diphenyldibiphenyl	Phenylarsine	Biphenyl-Mg-bromide	124–126
Di-*p*-anisyldibiphenyl	Anisylarsine	Biphenyl-Mg-bromide	Oil
Tetra-*p*-tolyl	Tolylarsine	Tolyl-Mg-bromide	108
Tetra-p-anisyl	Anisylarsine	Anisyl-Mg-iodide	128–129
Tetra-a-naphthyl	Naphthylarsine	Naphthyl-Mg-bromide	250–251

[a] Michaelis, footnote a, Table II, prepared the substance by the hydrolysis of the chloride, which had been obtained by heating phenyldichloro-arsine with an excess of ditolyl-mercury. He described it as being an oil.

Summary

1. The preparation of diphenyl, di-*p*-tolyl, di-*p*-anisyl and di-α-naphthyl mercury from the interaction of an arylmagnesium halide and mercuric chloride has been described.

2. Phenyl-, *p*-tolyl-, *p*-anisyl- and a-naphthylarsine oxide have been prepared. Two methods of preparation were used: (a) the diaryl mercury compound was heated with arsenic trichloride and the aryldichloroarsine formed was hydrolyzed; (b) the arylarsonic acid was reduced with sulfur dioxide in the presence of hydrochloric acid and the aryldichloroarsine was hydrolyzed.

3. A number of tetra-arylarsyl oxides of the type RR'As—O—AsR'R were prepared from the interaction of an arylarsine oxide and an arylmagnesium halide. In addition several mixed diarylarsinic acids and mixed diarylarsyl chlorides have been described.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, THE PENNSYLVANIA STATE COLLEGE]

CLEAVAGE OF AZO DYES BY MEANS OF SULFITES. THE CLEAVAGE OF 4-HYDROXY-AZOBENZENE-5-CARBOXYLIC ACID AND OF 3-METHYL-4-HYDROXY-AZOBENZENE-5-CARBOXYLIC ACID

BY KARL H. ENGEL

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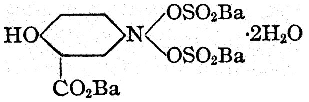
It has been reported in THIS JOURNAL[1] that azo dyes suffer a distinctive cleavage when heated with aqueous sulfite solutions. In a further study of this reaction, the behavior of the above-mentioned dyes has been investigated. The cleavage of these dyes followed closely the reaction course of 4-hydroxy-azobenzene: the primary dye component yielded aniline and an N-sulfonic acid of aniline, the secondary components N-mono- and N-disulfonic acid derivatives of salicylic and of o-cresotinic acids, respectively.

4-Hydroxy-azobenzene-5-carboxylic acid yielded an interesting N-disulfonic acid which could be isolated in pure form, as its tribarium salt, represented, presumably, by the formula



This compound was rather difficultly soluble and perfectly stable in neutral or alkaline solution. It rearranged, in the presence of mineral acids, in a

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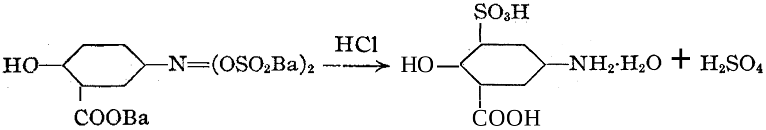
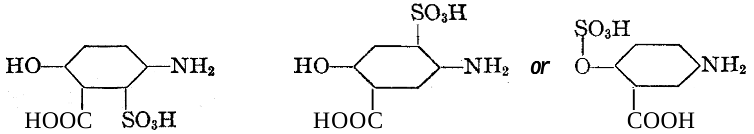
[1] Engel, THIS JOURNAL, 51,2986 (1929).

definite and clear cut way, yielding, quantitatively, the difficultly soluble aminosulfosalicylic acid, which may also be obtained by direct sulfonation of aminosalicylic acid.



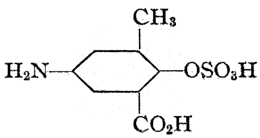
The N-monosulfonic acid, which was obtained in a smaller yield, differed strikingly from the N-disulfonic acid. It was extraordinarily soluble, sensitive to light and to air oxidation. Its free acid rearranged into an extremely soluble sulfonic acid derivative of aminosalicylic acid which could be diazotized and coupled with secondary azo components. It could possess one of the following structures

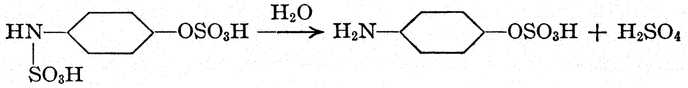


The first two formulas appeared highly improbable (especially the first), in view of the generally observed resistance of *p*-aminophenols to sulfonation in the *m*-position to the hydroxyl group. Since the reduction products of 4-hydroxy-azobenzene yielded the extremely soluble sulfonic ester of 1-amino-\$-phenol and no trace of the isomeric 1-amino-4-phenol-6-sulfonic acid, it might be concluded that the dye under investigation yielded a similar product, represented by the third formula.

The decided difference between the N-sulfonic acids, their strikingly reversed solubility relations, may be cited in support of a previously developed view that the N-disulfonic acids encountered in cleavage experiments should be looked upon as sulfurous esters of a substituted o-nitrous acid, N-monosulfonic acids as derivatives of amines, or true "sulfaminic" acids.

The cleavage of 3-methyl-4-hydroxy-azobenzene-5-carboxylic acid was investigated for a theoretical and a practical end. It was hoped that this dye, like its simpler homolog, would yield an N-disulfonic acid amenable to isolation in the form of its barium or lead salt, a hope which was not fulfilled. It was furthermore reasoned that such a product, of which a fair yield could be expected, might hydrolyze instead of yielding a nuclear sulfonic acid, the usual rearrangement, sulfonation in o-position to the hydroxyl group being prevented by the presence of substituents. The expected product, aminocresotinic acid, economically made, would be a useful dye intermediate. These premises proved correct to some extent; 18% of the theoretically possible yield of the desired substance was actually obtained. Unfortunately, for the economic aspects, the larger part of the N-disulfonic acid reacted in a third, and not completely unexpected, way, yielding the stable and extremely soluble sulfonic ester of aminocresotinic acid: a dye intermediate of much smaller value. The N-disulfonic acid derived through cleavage of 4-hydroxy-azobenzene[1] furnished a parallel to this behavior. It yielded 1-amino-4-phenol-5-sulfonic acid and, to a smaller extent, a compound which retained both sulfonic acid groups at a lower temperature, but lost one of these on further heating (or on diazotization in the cold), yielding aminophenol sulfonic ester, the reaction presumably proceeding in the following way





Sulfate Formation During Cleavage.—The cleavage of 3-methyl-4-hydroxy-azobenzene-5-carboxylic acid resulted in the formation of a considerable amount of mineral sulfate, corresponding to 12.1% of the sulfite consumed, as compared with 3.4% in the case of the salicylic acid derivative, and with 1.2% in the cleavage of 4-hydroxy-azobenzene. It was observed, as a general rule, applying to hydroxy as well as to amino azo dyes, that compounds which contained highly reactive secondary components (capable of coupling in the presence of a considerable hydrogen-ion concentration) yielded negligible amounts of sulfate, about 1%. On the other hand, dyes with weak secondary components, which coupled only in alkaline solutions, invariably yielded higher percentages. Reaction temperatures above 100° caused a considerable increase in sulfate formation, particularly in the latter class of dyes.

Increased sulfate formation did not lead to a gain in totally unsulfonated products, but to a decrease of N-disulfonic acids of the secondary components, reflected in a decrease in yield of their typical acid rearrangement products. Since the N-disulfonic acids, once formed, appeared resistant to prolonged heating at the reaction temperatures employed, it could be concluded that sulfate formation was due to hydrolysis of the first-formed sulfonic acid of the hydrazo bodies.

Experimental

Preparation of the Pure Dyes.—The sodium salts of the crude dyes were prepared by the usual coupling reactions, and the free dye acids by addition of acetic acid to solutions of the recrystallized sodium salts. The dried products were insoluble in alcohol, acetone or benzene, but became readily soluble in these solvents after a single recrystallization from 90% acetic acid. They also possessed sharp melting points then, whereas they charred without softening before recrystallization. The dyes were repeatedly recrystallized from ethyl alcohol. **4-Hydroxy-azobenzene-5-carboxylic** acid was found to melt at 220.5°, corr.

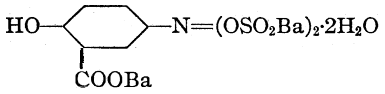
Anal. Calcd. for $C_{13}H_{10}O_3N_2$: N, 11.59. Found: N, 11.50.

3-Methyl-4-hydroxy-azobenzene-5-carboxylic acid melted at 202.0" corr.

Anal. Calcd. for $C_{14}H_{12}O_3N_2$: N, 10.96. Found: N, 10.92.

Cleavage of 4-Hydroxy-azobenzene-5-carboxylic Acid.—Twenty-four and twenty hundredths g. of the pure dye (0.1 mole) dissolved in water, the requisite amount of ammonia to form the ammonium salt, and ammonium sulfite equivalent to 420.2 cc. of 1 N solution (a total volume of 320 cc.) were heated in a nitrogen-filled pressure bottle at 90 to 93°. Decolorization was complete after six hours. This experiment, for quantitative determinations, was carried out in duplicate; the bottle contents were diluted accurately to 500 cc. Larger quantities of reagents (0.5 mole of the dye) were heated under identical conditions in a closed iron container. A qualitative separation of cleavage products from the resulting solution was attempted.

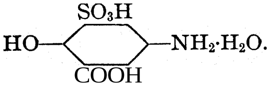
Isolation of Cleavage Products.—Aniline, which had formed as a result of the cleavage, was removed by benzene extractions. One equivalent of barium hydroxide, in solution, was then added for every sulfite equivalent originally present; precipitated barium sulfate and sulfite were removed by filtration of the hot suspension. The filtrate was evaporated to about 1200 cc. under a current of carbon dioxide, and additional precipitate again removed. On standing the clear filtrate yielded a heavy white precipitate of uniform composition. It was isolated and recrystallized from hot water. It was found to be the tribarium salt of an N-disulfonic acid derived from the secondary dye component, and may be assigned the formula



$$HO{-}C_6H_3(COOBa){-}N{=}(OSO_2Ba)_2\cdot 2H_2O$$

Anal. Calcd. for $C_7H_4O_9NS_2Ba_3\cdot 2H_2O$: N, 2.55: S, 11.62; Ba, 37.25. Found: N, 2.43; S, 11.49; Ba, 37.05. Calcd. for $2H_2O$, 6.52; loss on drying, 6.76. (The material was dried under a current of nitrogen at 120". It regained its original weight when exposed to the atmosphere.)

It tended to form clusters of microscopic crystals, short rods, apparently belonging *to* the rhombic system. The substance was capable of reducing ammoniacal silver solution but was quite resistant to air oxidation, even in solution. It produced, at great dilutions, a deep violet blue or prune coloration with ferric chloride and acetic acid. Addition of mineral acid caused rearrangement into **aminosulfosalicylic** acid,



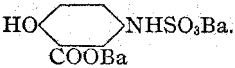
$HO{-}C_6H_2(SO_3H)(COOH){-}NH_2\cdot H_2O$. This compound was practically insoluble in cold but readily soluble in hot water. It was identical in composition and crystal habit and in **its** ferric chloride and diazo reactions, with the product obtained by direct sulfonation of **1-amino**-4-hydroxybenzene-5-carboxylic acid.

Anal. Calcd. for $C_7H_7O_6NS\cdot H_2O$: N, 5.58; S, 12.77; H_2O, 7.17. Found: N, 5.53; S, 12.78; loss on drying (over P_2O_5), 7.37.

The yield of this product from 3.000-g. portions of the tribarium salt was quantitative, 1.347 g. (theoretically possible, 1.365 g.).

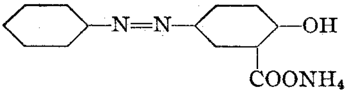
Phenylsulfaminic Acid, Barium Salt.—The mother liquor of the tribarium salt, described above, contained additional amounts of that product, which was precipitated by an equal volume of acetone. The filtered acetone solution was then evaporated to 200 cc.; to the remaining aqueous solution was added 500 cc. of methanol which precipitated the barium salt of phenylsulfaminic acid, $C_6H_5NHSO_3Ba$. This was isolated by filtration, washed with methanol and directly analyzed. It yielded aniline and sulfuric acid in the presence of hydrochloric acid. In solution, it was sensitive to air oxidation.

Anal. Calcd. for $C_6H_6O_3NSBa$: N, 5.83; S, 13.32; Ba, 28.47. Found: N, 5.62; S, 13.04; Ba, 28.61.

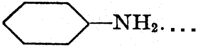
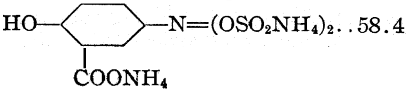
The alcoholic mother liquor, after concentration to a small volume, deposited mixtures of barium salts, which, on addition of acids, yielded both aniline and an extremely soluble salicylic acid derivative. Presumably the mixture contained the barium salt of the N-monosulfonic acid derived from the secondary dye component,  It was quite sensitive to air oxidation. Ferric chloride caused a claret-red coloration.

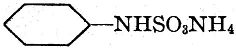
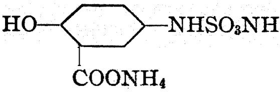
Quantitative examinations of the 500-cc. solutions, containing a tenth mole of dye, were made in the manner described for 4-hydroxy-azobenzene.' Aniline, recovered by benzene extractions, required 65.0 and 65.4 cc. of normal nitrite solution, a yield of 65.2% of the theoretical. An excess of 26.6 cc. of 1 *N* sulfite solution was found present after cleavage; 393.6 cc. of a normal, or 196.8 cc. of a molar solution of sulfite was therefore consumed, or 1.968 mole to one mole of dye. Sulfate formed during cleavage corresponded to 1.596 g. of barium sulfate, equivalent to 13.7 cc. of 1 N sulfite solution or to 3.4% of the consumed sulfite. No totally unsulfonated derivative of the secondary dye component could be detected.

Upon the preceding determinations the following tabulation of products and yields could be based.

CLEAVAGE OF THE DYE 

From primary component **From secondary component**

Ia  65.2% IIa  58.4%

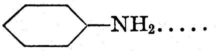
Ib  34.8% IIb  41.6%

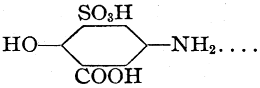
Two hundred and fifty-cc. portions (0.05 mole of dye) were heated to 95° and acidified with 60 cc. of concd. hydrochloric acid, thus causing decomposition of phenylsulfaminic acid (Ib) into aniline and sulfuric acid, rearrangement of the N-disulfonic acid (IIa) into nuclear aminosulfosalicylic acid with incidental hydrolysis of one of its sulfonic acid groups, and rearrangement of the N-monosulfonic acid (IIb) into the extremely soluble sulfonic ester of aminosalicylic acid. The aniline liberated and isolated required 16.3 cc. of 1 N nitrite solution; 7.253 g. of aminosulfosalicylic acid ($1H_2O$) was isolated. Diazotization of the remaining soluble aminosalicylic acid derivative consumed 20.2 cc. of 1 N nitrite solution. The product itself could not be induced to crystallize from its solution. It was quite resistant toward hydrolytic action of strong acids. Prolonged heating at 100° in the presence of about 5 M hydrochloric acid solution caused some decomposition but no appreciable sulfuric acid formation. The diazonium derivative was coupled with 1-naphthylamine in the presence of acetate and acetic acid. The resulting brown dye was insoluble, in the form of its free acid, and permitted quantitative isolation. Nitrogen and sulfur determinations showed the presence of one sulfonic acid group in the dye molecule.

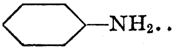
Anal. Calcd. for $C_{17}H_{13}O_6N_3S$: N, 10.87; S, 8.28. Found: N, 10.67; S, 8.03; sulfated ash, none.

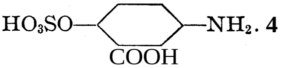
Azo dyes differed very little in dyeing shades from corresponding azo derivatives of the nuclear aminosulfosalicylic acid. They did possess greater solubility.

ACTUAL YIELDS OF FINAL USEFUL PRODUCTS FROM REARRANGEMENT OF PRODUCTS TABULATED ABOVE

Ia  $C_6H_5-NH_2$..... 65.2%

IIa →  $HO-C_6H_2(SO_3H)(COOH)-NH_2$.....57.8%

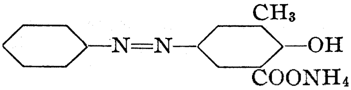
Ib →  $C_6H_5-NH_2$..32.6%

IIb →  $HO_3SO-C_6H_3(COOH)-NH_2$. 40.4%

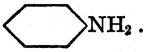
Cleavage of 3-Methyl-4-hydroxy-azobenzene-5-carboxylic Acid.—Portions of one tenth mole of dye, 25.622 g., an equivalent amount of ammonia for its solution and ammonium sulfite corresponding to 419.6 cc. of 1 N solution, contained in about 320 cc. of water, were heated in closed nitrogen-filled bottles at 90 to 93°. The dye was reduced with exceptional ease, three hours of heating being sufficient. The solutions were diluted to 500 cc., accurately, and analytical determinations made as described before.

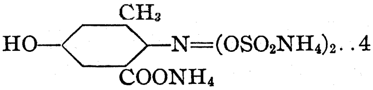
Aniline, extracted with benzene, consumed 66.0 cc. of 1 N nitrite solution for diazotization. N-sulfonic acids remaining in solution could not be induced to crystallize from solution either as calcium, barium or lead salts. Their solution was quite sensitive to air oxidation. Dilute ferric chloride caused a transient reddish-blue coloration.

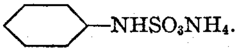
Determination of unconsumed sulfite showed the presence of 27.9 cc. of 1 N solution; 391.4 cc. of 1 N or 195.7 cc. of a molar solution was therefore used, or slightly less than two moles of sulfite to one of dye. Sulfate generated during cleavage was determined in 25-cc. portions of the ammoniacal solution. 0.2810 g. of barium sulfate was found, or 5.620 g. in 500 cc. of the original solution, corresponding to 48.2 cc. of 1 *N* solution, or to 12.1% of the sulfite consumed. Dilute acetic acid added to the cold solution of cleavage products did not cause a precipitate. Totally unsulfonated aminocresotinic acid, which is difficultly soluble, therefore, could not have been present. On these various determinations may be based the following tabulation of primary cleavage products and their approximate yields.

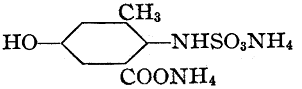
CLEAVAGE OF THE DYE  $C_6H_5-N{=}N-C_6H_2(CH_3)(COONH_4)-OH$

From primary component **From secondary component**

Ia  $C_6H_5NH_2$..........66.0%

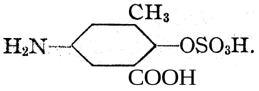
IIa  $HO-C_6H_2(CH_3)(COONH_4)-N{=}(OSO_2NH_4)_2$..41.8%

Ib  $C_6H_5-NHSO_3NH_4$..34.0%

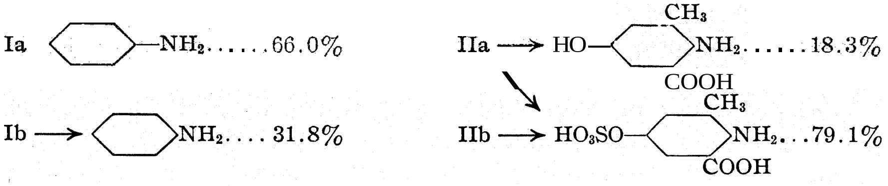
IIb  $HO-C_6H_2(CH_3)(COONH_4)-NHSO_3NH_4$ 48.2%

Decomposition and Rearrangement of N-sulfonic Acids.—Addition of an excess of mineral acid to the hot solution of cleavage products caused decomposition of the primarily formed phenylsulfaminic acid, aniline corresponding to 31.8 cc. of 1 *N* nitrite solution and sulfuric acid being formed. The secondary component yielded two products: aminocresotinic acid and an extremely soluble monosulfonic acid derivative of the same compound. One-tenth mole of dye yielded 3.052 g. of aminocresotinic acid, or 18.3% of the theoretically possible amount.

Anal. Calcd. for $C_8H_9O_3N$: N, 8.40; acidity, 1.0000 g. = 5.983 cc. of 1 *N* NaOH solution. Found: N, 8.26; acidity (electrometric titration with 0.1 N NaOH), 1.0000 g. = 5.830 cc. of 1 N NaOH.

The sulfonated aminocresotinic acid differed distinctly in solubility and crystal habit from the product obtained through direct sulfonation of aminocresotinic acid. It appeared highly probable, therefore, that the rearrangement product was not a nuclear sulfonic acid but a phenol ester . Diazotized and coupled with azo components, this compound yielded dyes which differed from corresponding azo derivatives of aminocresotinic acid and of its nuclear sulfonic acid by a visible shift toward absorption in regions of longer wave lengths. Diazotization of the sulfonic ester of aminocresotinic acid, originating from one-tenth mole of dye, required 79.1 cc. of 1 N nitrite solution.

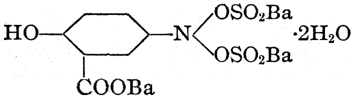
REARRANGEMENT OF N-SULFONIC ACIDS TABULATED ABOVE (ACTUAL YIELDS)

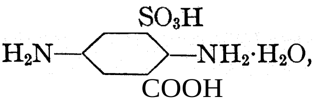
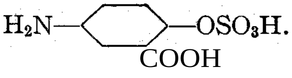
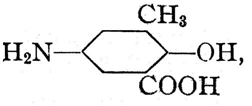
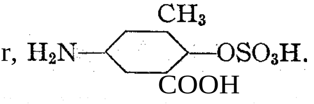


Summary

1. The sulfite cleavage of 4-hydroxy-azobenzene-5-carboxylic acid and of its 3-methyl homolog has been investigated.

2. A difficultly soluble barium salt of an N-disulfonic acid derived from 1-amino-4-hydroxybenzene-5-carboxylic acid could be isolated in pure form. Its distinctive reactions substantiated a newly proposed formulation for N-disulfonic acids as, for example



3. Hydrolysis and rearrangement of N-sulfonic acids resulted in complete re-formation of the primary dye component, aniline. The secondary component of the first dye yielded aminosulfosalicylic acid, , and the sulfonic ester, . The secondary component of the other dye yielded aminocresotinic acid, , and its sulfonic ester, .

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

STRUCTURE OF METHYLATED SUGARS. I. PRELIMINARY PAPER

BY CARRELL H. WHITNAH

RECEIVED JULY 1, 1929 PUBLISHED NOVEMBER 8, 1929

The recognized conflict of the results obtained by C. S. Hudson,[1] by comparing differences of optical rotations of sugars, with the results of W. N. Haworth and co-workers[2] from the properties of methylated sugars, suggests the possibility that the ring structure of glucose may be changed by the processes used to establish it.

The possibility of variation of the ring structure of methylated sugars with the temperature and alkalinity of methylation is suggested by the convincing evidence that "normal" or "abnormal" glucoside rings are formed on condensation of sugars with alcohol containing small amounts of hydrogen chloride at high[3] and low[4] temperatures, respectively.

The production of "normal" glucoside at low temperature in alcohol containing more acid[5] indicates the importance of the alkalinity factor.

The care deemed necessary by Hibbert[6] in drawing conclusions as to carbohydrate structure from methylation experiments, carried out in "slight hydrogen-ion concentrations," and the indications[7] that more than one ring structure is formed on methylation of galactose and arabinose with methyl sulfate and sodium hydroxide, justify the attempt to find conditions under which glucose will yield a methylated product of unusual structure.

Experimental Part

Twenty grams of glucose was dissolved in 25 cc. of water and placed in a bath at thirty degrees. The solution was made alkaline with sodium hydroxide and then fifteen to twenty cc. of methyl sulfate added Thirty per cent. sodium hydroxide was then added a drop at a time so as to maintain the solution alkaline to brom thymol blue but acid to phenolphthalein One cc. of 30% sodium hydroxide eventually neutralized about an equal volume of methyl sulfate. The alkalinity was determined by dropping a drop of the reaction mixture into a drop of indicator on a spot-plate. A much more sensitive and convenient indicator of alkalinity was a simple potentiometer attached to a cell made by suspending in the reaction mixture electrodes of platinum and antimony. The potentiometer determinations required occasional checking against the determina-

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[1] C. S. Hudson, THIS JOURNAL, **48,** 1434 (1926).

[2] (a) E. L. Hirst, J. *Chem. Soc., 350* (1926); (b) W. N. Haworth and C. W. Long, *ibid., 345* (1929); (c) W. N. Haworth and S. Peat, *ibid.,* 350 (1929).

[3] (a) E. Fischer, *Ber.,* **28,** 1145 (1895); (b) T. S. Patterson and J. Robertson, *J. Chem. Soc., 300* (1929).

[4] E. Fischer, *Ber.,* **47,** 1980 (1914).

[5] E. Fischer, *ibid.,* 26, 2400 (1893).

[6] H. Hibbert and N. M. Carter. THIS JOURNAL, **51,** 1601 (1929).

[7] E. L. Hirst and G. J. Robertson, J. *Chem. Soc.,* **127, 358** (1925).

tions with color indicators, as the potential corresponding to a given alkalinity changed slowly with the composition of the solution.

More methyl sulfate was added from time to time so that there was an excess of at least 10 cc. over the sodium hydroxide added.

From 30 to 35 cc. of sodium hydroxide was added during from eight to ten hours before the mixture ceased to reduce Fehling's solution. The alkalinity and temperature were then somewhat increased and thereby the rate of methylation. The reaction was stopped when 100 cc. of methyl sulfate had been used up and the bath finally was heated to about 70° to insure destruction of all of the methyl sulfate. Tests for active sugar have not been obtained from any experiment in which the final destruction of methyl sulfate was carried out in a boiling water-bath.

After cooling, the sugar solution was extracted with chloroform, the extract dried over calcium chloride, the chloroform evaporated and the residue distilled at about 2-mm. pressure and at temperatures always over 100°. The distillate when dissolved in water, acidified with hydrochloric acid and treated with barium chloride, showed no trace of sulfate even after standing for several days.

The first test used to demonstrate the presence of active glucoside was to decolorize a few drops of dilute permanganate with a few drops of the product dissolved in water. One-tenth gram of methylated sugar would completely decolorize three drops of permanganate within one minute, while a similar solution of ordinary methylated glucose retained the color of one drop of permanganate for several minutes. **A** more definite comparison of rates of oxidation is indicated by Table I and the curves of Fig. 1.

TABLE I

EXPERIMENTAL DATA

Subs. obs.	A	B	C	D
Used, g.	0.090	0.060	0.150	0.096
Time, min.	0.067 N $KMnO_4$ per 0.100 g. of subs., cc.			
1				0.21
2				.42
3		0.05		
4	0.17	.09		
6.5			0.20	
7		.13	.27	1.60
8.5	.25			
11			.54	2.63
14				3.07
15			.95	
18	.33		1.42	3.54
21			2.03	
22				3.82
24		.55	2.26	
26		.60		
29		.83		
32			2.53	
31				4.31
36		1.00		
37.5			2.60	
40				4.75
44		1.21		
46			2.66	
48				5.16
50.5		1.39		
55			2.70	
58		1.60		5.56
68.5		1.81		
72				6.13
77.5		2.00		
81				6.51
90		2.25		6.91
97.5		2.45		
104		2.78		7.44
118	0.79 (interpolated)			
307	1.66 (not completely reduced)			

The substances examined include **(A)** a stable methylated glucoside obtained by methylating at 60° in a solution of about 0.025 N sodium hydroxide; (B) glucose; (C) the methylated glucoside prepared above; and (D) a solution made by hydrolyzing this glucoside in 0.10 N hydrochloric acid and then neutralizing with sodium hydroxide.

The weight of the substance indicated was dissolved in 50 cc. of water and made neutral to litmus. The permanganate solution was then added as required. Except for the last observation on substance (A), each addition of permanganate was one drop as soon as the solution failed to depolarize a cell made by inserting electrodes of silver and platinum in the solution.[8]

Other tests to prove the existence of active sugar depend on the possibility of hydrolysis with dilute hydrochloricacid. Ready hydrolysis in a boiling water-bath was indicated by the increase of specific rotation of 1.2 g. of substance in 15.00 cc. of 0.10 *N* hydrochloricacid, from 32.7" to 65° in three hours.

On standing overnight at room temperature after two hours in a boiling water-bath, the specific rotation rose from 61.7" to 90.8°. The final value at room temperature, after the rotation in a boiling water-bath became constant at 67.8°, was 112.5".

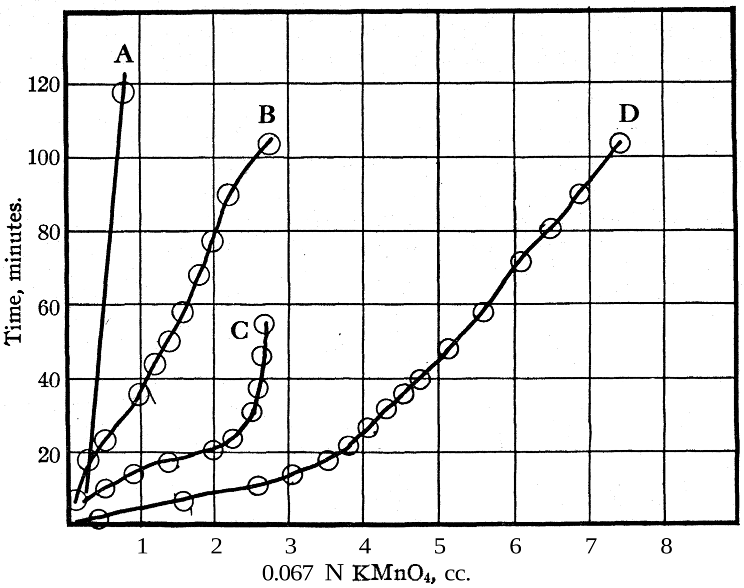

Fig. 1.

Hydrolysis at 60° was indicated by the fact that 1 g. of substance in 10 cc. 0.10 *N* hydrochloric acid increased its capacity for oxidation by iodine[9] from an initial value of 0.24 g. of iodine to 1.10 g. after three and one-half hours and to 1.37 g. after twenty-one hours. Corresponding values for α-methylglucoside were from an initial value of 0.187 g. of iodine to 0.382 g., after three and one-half hours, and 0.536 g. after twenty-one hours.

For both glucosides, hydrolysis with 8% or 2.14 N hydrochloric acid finally produced a decreasing iodine capacity. The values for the active glucoside were 0.64 g. of iodine after one and seven-tenth hours, 0.312 g. after three and one-half hours and 0.147 g. after twenty-one hours.

The relative rates of hydrolysis at 60° were also indicated by the fact that the above solution of active methylated glucoside after hydrolysis with 0.10 N hydrochloric acid had to be diluted about nine times as much as the similar solution of α-methylglucoside

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[8] B. F. Brann and M. H. Clapp, THIS JOURNAL, 51, 39 (1929).

[9] H. Sobotka, *J. Biol. Chem.*, **69**, 267 (1926).

in order that equal volumes of the two solutions would completely reduce equal volumes of Fehling's solution.

Summary

Methylation of glucose with methyl sulfate and sodium hydroxide at a temperature of 30° in a solution kept alkaline to brom thymol blue and acid to phenolpthalein resulted in a product which definitely gave a positive response to several common tests for an active or gamma sugar.

MANHATTAN, KANSAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF TRIPHENYLMETHYLMAGNESIUM CHLORIDE

BY HENRY GILMAN AND E. A. ZOELLNER

RECEIVED JULY 2, 1929 PUBLISHED NOVEMBER 8, 1929

Introduction

In connection with studies[1] involving triphenylmethylmagnesium chloride, it was necessary to develop a procedure for the preparation of this Grignard reagent in consistently high yields. We have had indifferent success, for some time, in preparing this reagent by methods commonly employed for the preparation of typical RMgX compounds.

The method described at this time gives excellent yields (96% and higher). These yields have been checked by different workers in this Laboratory so that the preparation is not as erratic as formerly. Our acid method of titration was used in determining the optimal factors reported at this time. The method of titration is very probably sound, and the high yields are unquestionably real because carbonation of the triphenylmethylmagnesium chloride has given yields of triphenylacetic acid as high as 91%.[2]

Experimental Part

The general procedure followed was that described recently by Gilman, Zoellner and Dickey[3] for the determination of yields of a variety of Grig-

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[1] (a) Gilman and Jones, THIS JOURNAL, 51, 2840 (1929); (b) Gilman and Fothergill, *ibid.*, 51, 3149 (1929).

[2] Unlike some other directions on optimal conditions for the preparation of unusual Grignard reagents reported from this Laboratory [such as allylmagnesium bromide by Gilman and McGlumphy, *Bull. soc. chim.*, 43, 1322 (1928), and *tert.*-butylmagnesium chloride and *tert.*-amylmagnesium chloride by Gilman and Zoellner, *Rec. trav. chim.*, 47, 1058 (1928)], considerable work has been done by others on triphenylmethylmagnesium chloride, particularly in connection with free radicals. Among such earlier work are the following important references: Schmidlin, Ber., 39, 628, 4183 (1906), and Chichibabin, *ibid.*, 40, 3965 (1907); *ibid.*, 42, 3469 (1909). These authors have reported unusually high yields of products from triphenylmethylmagnesium chloride.

[3] Gilman, Zoellner and Dickey, THIS JOURNAL, 51, 1576, 1584 (1929).

nard reagents. Before describing a typical experiment for the preparation of triphenylmethylmagnesium chloride, a short discussion will be given of the effect of some factors on the yield of this Grignard reagent.

The quantities of materials used in our present optimal conditions (in the titration studies) were as follows: 2.79 g. (0.01 mole) of triphenylchloromethane, 0.5 g. (0.021 atom) of magnesium of 80–200 mesh; 0.32 g. (0.025 atom) of iodine, and 40 *cc.* (0.39 mole) of anhydrous ether. The equivalent molecular (or atomic) ratios of these reactants are 1.0 of triphenylchloromethane, 2.1 of magnesium, 0.25 of iodine and 39.0 of ether.

Halide.—The triphenylchloromethane as finally used was the pure compound obtainable from the Eastman Kodak Company. Despite the fact that some of the samples have a distinct odor of hydrochloric acid, the chloride evidently is of high purity for the present purpose. Samples of the chloride frequently contain two distinct kinds of crystals, white and yellow, each variety melting at **110–112".** Experiments were carried out with samples of each and no essential difference in yield was noted.

Magnesium.—The magnesium was of **80–200** mesh. Ordinary magnesium turnings may be used, but optimal yields (under our conditions) with such magnesium require that **1.5** g. or **6.3** atom equivalents (instead of **2.1** with the **80–200** mesh magnesium) be taken. The yield varies with the quantity of magnesium **(80–200** mesh), decreasing with small quantities of magnesium. It should be understood that the reacting ratio of magnesium is greater than one, inasmuch as a part of the **2.1** atom equivalents is used up not only by the triphenylchloromethane but also by the **0.25** equivalent of iodine. Several experiments with **30–80** mesh magnesium showed no essential difference in yield.

Iodine.—The iodine was dried in a desiccator over sulfuric acid and need not, of course, be powdered. The quantity of iodine has a marked effect on the yield. A progressive decrease in yield, under our conditions, was noted when less than **0.25** atom equivalent of iodine was used. Apparently, the yield is not improved by using more than **0.25–0.30** atom equivalent of iodine. The function of the excess magnesium and excess iodine in this preparation is made clear in the preliminary paper by Gilman and Fothergill[1b] on the dissociation of triphenylmethylmagnesium chloride. Actually, when the triphenylmethylmagnesium chloride is prepared by means of this relatively large quantity of iodine, there may be present, at the end of the reaction, some triphenylmethylmagnesium iodide.'

Ether.—The ether must be dry. Ether dried over sodium and kept over sodium was found to produce a turbidity in the mere transferal on a *humid* day. On such days the ether was distilled from sodium directly into the special reaction flask[3] for our quantitative studies. This extra refinement is unnecessary for ordinary purposes. The **39** molecular equivalents used in our determinations is unquestionably greater than that required. Ordinarily no more than 6–8 equivalents of ether are needed for the preparation of Grignard reagents.[2,3] This large quantity was used to prevent the triphenylchloromethane from splashing on the sides of the flask and so being removed, in part, from reaction with the magnesium. The large quantity of ether is desirable in effecting reactions of this Grignard reagent because of its sparing solubility in ether.

The benzene used to dissolve the RMgX compound so that aliquots could be removed for titration was dried over sodium. Such solution is unnecessary in the carbonation leading to the preparation of triphenylacetic acid, and the high yields of acid were obtained from the suspension of the RMgX compound in ether. However, the

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[4] Gilman and St. John, *Rec. trav. chim., 48 (1929).*

benzene-ether solution of triphenylmethylmagnesium chloride may be desirable, if not necessary, for the preparation of other compounds from this Grignard reagent. Also, solution in an ether–benzene mixture may be necessary in separating the Grignard reagent from the excess of magnesium, for special reactions wherein the magnesium is harmful.

Atmosphere.—All experiments were carried out in an atmosphere of pure dry nitrogen. In both of the larger-sized runs in which triphenylacetic acid was prepared and in the smaller analyses the trap of Gilman and Hewlett[6] was found eminently satisfactory and made it possible to dispense with a continuous stream of inert gas

Preparation of Triphenylmethylmagnesium Chloride.—The 0.01 mole runs were carried out in special flasks of the kind described recently.[3] The 0.02 mole run was carried out in a 200-cc, and the 0.04 mole preparations in a 500-cc. three-necked flask provided with a mercury-sealed stirrer and a spiral water condenser the top of which was attached directly to the trap[6] after the flask was swept out by a stream of dry and oxygen-free nitrogen or hydrogen.

The magnesium, ether and iodine are added to the carefully dried flask, and when all of the iodine has reacted with the magnesium (as indicated by the disappearance of the iodine color)[6] the triphenyichloromethane is added as a solid and at one time. Partial solution is effected, during stirring, by directly heating the flask with a small flame for a few moments. With such heating a spontaneous reaction sets in, and as the halide reacts an insoluble complex forms. The reaction mixture is then refluxed moderately (in our experiments by heating with an electric hot-plate) for three hours.[7]

The following series of color changes occurs under anhydrous conditions during the course of heating. First, the greenish-yellow solution resulting on dissolution of the chloride turns brown about ten or fifteen minutes after the initial heating. Then, after thirty to forty minutes the solution becomes reddish-brown and the mixture contains little if any precipitate. During the next five or ten minutes the quantity of buff or fawn-colored precipitate increases markedly, and in some cases with distinct suddenness. The quantity of precipitate increases up to one and one-half hours of refluxing and then completely fills the solvent.[8] With refluxing beyond one and one-half hours the volume of precipitate frequently decreases somewhat. At the end of the three-hour (total) period of refluxing, the reaction is done,[9] and can be used directly for the prepa-

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[5] Gilman and Hewlett, *Rec. trav. chim.*, 48 (1929). By regulation of the trap it is an easy matter to distil off ether and replace it by benzene (or another solvent) without a continuous flow of inert gas.

[6] Stirring is started at once and the iodine disappears in a few minutes. At this stage, if the reagents and apparatus were dried carefully, the solution has only a very slight turbidity and with special care it is entirely clear. When anhydrous conditions are not present the yield is decreased at least 4–5%.

[7] In the smaller 0.01 runs the time of heating was one and one-half hours plus the twenty to thirty minutes of heating during the removal of ether prior to the addition of benzene to get soluble aliquots for analysis. In either the 0.01, 0.02 or 0.04 mole runs a two-hour period of heating is sufficient to give an excellent yield by titration; however, our best yields of acid (from carbonation of the Grignard reagent) were obtained after a three-hour period of heating. The yield of acid drops about 7% with a one and one-half to two hour period of heating.

[8] It is partly for this reason that the large volume of ether is desirable in order to facilitate completion of reaction. If stirring is interrupted at this stage, the precipitate settles somewhat, revealing a thin upper ethereal layer of a reddish color.

[9] Should it be desirable to remove aliquots for titration or to dissolve the Grignard reagent for a special subsequent reaction, the ether is removed by heating with a hot

ration of triphenylacetic acid and other derivatives, particularly those which form ether-soluble magnesium complexes.[10]

Summary

Conditions have been determined for the preparation of triphenylmethylmagnesium chloride in excellent yields.

AMES, IOWA

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

THE REACTION BETWEEN ALKALI METAL ALKYLS AND QUATERNARY PHOSPHONIUM HALIDES

BY D. D. COFFMAN AND C. S. MARVEL

RECEIVED JULY 6, 1929 PUBLISHED NOVEMBER 8, 1929

The question of whether or not phosphorus ever has a valence of five is still open. It is generally accepted that in the phosphonium salts its valence is four and that the negative ion is held by a polar valence to the phosphonium ion. Lewis[1] believes that phosphorus shares five pairs of electrons with five chlorine atoms in phosphorus pentachloride and has therefore a valence of five. Langmuir[2] has said that the valence of phosphorus in this compound is four and that one chlorine atom is held by a polar valence. Prideaux[3] has presented the idea that three of the chlorine atoms are attached to the phosphorus atom by means of true covalences whereas the remaining two are joined by singlet linkages. Sugden[4] has advanced experimental evidence favoring this view.

Staudinger and Meyer[5] attempted to prepare penta-alkyl phosphorus compounds by the action of zinc ethyl on tetra-ethylphosphonium iodide. However, at low temperatures no reaction was noted and at higher temperatures they obtained triethylphosphine, butane and zinc iodide. The same investigators[6] have prepared the compound $(C_6H_5)_3P{=}C(C_6H_5)_2$, called by them triphenylphosphinediphenylmethylene, in which all of the valences of phosphorus are satisfied by carbon atoms. This compound

water-bath (60–80°). Then the addition of a volume of benzene in slight excess of that of the ether removed dissolves the reagent. For titration purposes it is merely necessary to make several marks on the reaction flask in order to measure subsequently the total volume of Grignard solution.

[10] Details will appear shortly on some general preparations involving triphenylmethylmagnesium chloride.

[1] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Company, New York, 1923, p. 102.

[2] Langmuir, THIS JOURNAL, 41, 919 (1919).

[3] Prideaux, *Chem. Industry,* 42, 672 (1923).

[4] Sugden, *J. Chem. Soc.,* 1174 (1927).

[5] Staudinger and Meyer, *Helv. Chim. Acta,* 2, 612 (1919).

[6] Staudinger and Meyer, *ibid.,* 2, 635 (1919).

was prepared by combining triphenylphosphine with diazodiphenylmethane to give a phosphazine which lost nitrogen when heated.

$$(C_6H_5)_3P + (C_6H_5)_2CN_2 \longrightarrow (C_6H_5)_3{-}P{=}N{-}N{=}C(C_6H_5)_2 \longrightarrow (C_6H_5)_3P{=}C(C_6H_5)_2 + N_2$$

The phosphinemethylene resembled in many respects the tetramethyltriphenylmethylammonium, which was prepared previously by Schlenk and Holtz.[7] It is a brilliant red compound which is sensitive to air and moisture. With water it gives triphenylphosphine oxide and diphenylmethane, and with acids the corresponding phosphonium salt. Two of Staudinger's students, Lüscher[8] and Isler[9] have obtained some phosphinemethylenes by the action of molten potassium on quaternary phosphonium salts.

$$2R_3PBr{-}CHR_2 + 2K \longrightarrow 2R_3P{=}CR_2 + 2KBr + H_2$$

Only the compound containing five phenyl groups was stable enough for isolation in the pure form although certain others were formed in solution.

In the hope of gaining further knowledge concerning the valence of phosphorus, the reactions of alkali metal alkyls with phosphonium salts have been investigated. Two alkali metal alkyls, lithium n-butyl and sodium triphenylmethyl, have been used. The first phosphonium salt studied was tetra-ethylphosphonium iodide. The reaction of this compound with sodium triphenylmethyl ran smoothly at ordinary temperatures. The color of the sodium triphenylmethyl faded and on working up the reaction mixture triphenylmethane, triethylphosphine and sodium iodide were obtained. This reaction is exactly analogous to the reaction between tetra-ethylphosphonium iodide and zinc ethyl reported by Staudinger and Meyer.[5] It is also analogous to the reactions of quaternary ammonium salts with alkali metal alkyls which have been studied by Hager with Marvel.[10]

Preliminary experiments with triphenylalkylphosphonium halides and alkali metal alkyls seemed to give colored solutions or colored insoluble compounds which resembled the phosphine methylenes. Accordingly, triphenyldiphenylmethylphosphonium bromide was prepared and treated with lithium n-butyl and with sodium triphenylmethyl. Both reagents produced triphenylphosphinediphenylmethylene in good yields. The reaction proceeds at room temperature and goes especially smoothly with lithium n-butyl.

The other phosphonium salts which were used were methyltriphenylphosphonium iodide, ethyltriphenylphosphonium iodide and *iso*propyltriphenylphosphonium bromide. These compounds reacted with an

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[7] Schlenk and Holtz, *Ber.*, 49, 603 (1916).

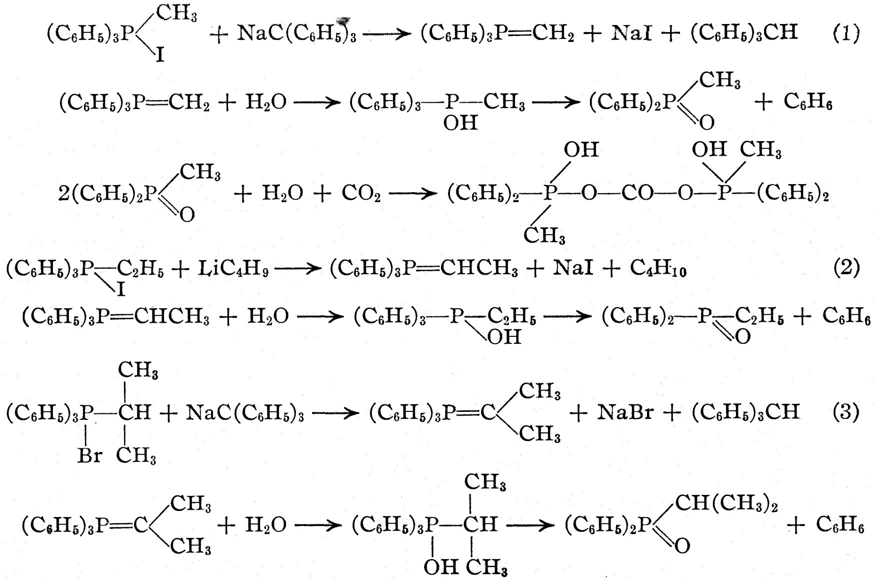
[8] Lüscher, Ph.D. "Thesis," Zurich, 1922.

[9] Isler, Ph.D. "Thesis," Zurich, 1924.

[10] Hager with Marvel, THIS JOURNAL, 48, 2689 (1926).

ether solution of sodium triphenylmethyl or lithium *n*-butyl to give colored solutions which decolorized on exposure to moist air. The products isolated after decomposition were, respectively, a derivative of methyldiphenylphosphine oxide, ethyldiphenylphosphine oxide and *iso*propyldiphenylphosphine oxide. The formation of these compounds can best be explained by assuming that a phosphinemethylene is the first product of the reaction between the alkali metal alkyl and the phosphonium salt. When moist air is admitted to the reaction mixture the phosphinemethylene is converted to the quaternary phosphonium hydroxide, which then decomposes to the diphenylalkylphosphine oxide and benzene.[11]

The following equations illustrate the steps in these reactions



$$(C_6H_5)_3P\begin{matrix}CH_3\\ I\end{matrix} + NaC(C_6H_5)_3 \longrightarrow (C_6H_5)_3P{=}CH_2 + NaI + (C_6H_5)_3CH \qquad (1)$$

$$(C_6H_5)_3P{=}CH_2 + H_2O \longrightarrow (C_6H_5)_3{-}\underset{OH}{P}{-}CH_3 \longrightarrow (C_6H_5)_2P\begin{matrix}CH_3\\ O\end{matrix} + C_6H_6$$

$$2(C_6H_5)_2P\begin{matrix}CH_3\\ O\end{matrix} + H_2O + CO_2 \longrightarrow (C_6H_5)_2{-}\underset{CH_3}{\overset{OH}{P}}{-}O{-}CO{-}O{-}\overset{OH\ CH_3}{P}{-}(C_6H_5)_2$$

$$(C_6H_5)_3P\begin{matrix}C_2H_5\\ I\end{matrix} + LiC_4H_9 \longrightarrow (C_6H_5)_3P{=}CHCH_3 + NaI + C_4H_{10} \qquad (2)$$

$$(C_6H_5)_3P{=}CHCH_3 + H_2O \longrightarrow (C_6H_5)_3{-}P\begin{matrix}C_2H_5\\ OH\end{matrix} \longrightarrow (C_6H_5)_2{-}P\begin{matrix}C_2H_5\\ O\end{matrix} + C_6H_6$$

$$(C_6H_5)_3\underset{Br}{P}{-}\underset{CH_3}{\overset{CH_3}{CH}} + NaC(C_6H_5)_3 \longrightarrow (C_6H_5)_3P{=}C\begin{matrix}CH_3\\ CH_3\end{matrix} + NaBr + (C_6H_5)_3CH \qquad (3)$$

$$(C_6H_5)_3P{=}C\begin{matrix}CH_3\\ CH_3\end{matrix} + H_2O \longrightarrow (C_6H_5)_3\underset{OH}{P}{-}\underset{CH_3}{\overset{CH_3}{CH}} \longrightarrow (C_6H_5)_2P\begin{matrix}CH(CH_3)_2\\ O\end{matrix} + C_6H_6$$

There was no indication in any of the reactions studied that a penta-alkyl phosphorus compound analogous to the penta-alkyl nitrogen derivative of Schlenk and Holtz[7] had been obtained. Neither was there any evidence of penta-alkyl phosphorus compounds in which five equivalent valences were combined with the organic radicals. The phosphinemethylenes which are represented as intermediates in all of the above reactions are probably not compounds in which phosphorus has a valence of five but rather resemble the amine oxides and phosphine oxides in their structure.

In all the phosphonium salts thus far studied there has been one group which carried a hydrogen atom on the carbon attached to the phosphorus atom. Some compounds are now being studied where this is not true,

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[11] Michaelis and Soden, *Ann.*, 229, 315 (1885).

and preliminary results indicate that penta-alkyl phosphorus compounds may thus be obtained.

Experimental Part

Sodium triphenylmethyl solution in dry ether was prepared according to the general method of Schlenk and Holtz.[7] The modified reaction flask shown in Fig. 1 allows easy separation of the solution of the metallic alkyl from the excess amalgam and sodium chloride. Lithium n-butyl was prepared by the method of Hager and Marvel.[10] The triphenylphosphine was obtained by the method of Dodanow and Medox[12] and the phosphonium salts were prepared as described by Lüscher[8] and by Michaelis and Soden.[13] The apparatus used in the reactions was similar to that described by Hager and Marvel.[10]

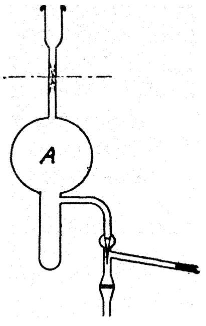

Fig. 1.

Lithium n-Butyl and Triphenyldiphenylmethylphosphonium Bromide.—The lithium n-butyl solution obtained by the action of 1.6 g of di-n-butyl mercury and 0.5 g. of lithium in petroleum ether was run onto 5 g. of triphenyldiphenylmethylphosphonium bromide. The colorless salt immediately turned bright red. After two days the reaction flask was opened, the reaction mixture was filtered and the red reaction product was separated from the unreacted phosphonium salt and sodium bromide by dissolving it in dry benzene. After several crystallizations the product was dried in an atmosphere of nitrogen over phosphorus pentoxide. The yield was 0.8 g. The product melted at 172–174° and all of its properties agreed with those ascribed to triphenylphosphine-diphenylmethylene by Staudinger and Meyer.[6] A mixture of this material and some made by the published method melted at 172–174°.

Anal. Subs. 0.2087: CO_2, 0.6645; H_2O, 0.1158. Calcd. for $C_{31}H_{25}P$: C, 86.91; H, 5.85. Found: C, 86.83; H, 6.16.

Sodium Triphenylmethyl and Triphenyldiphenylmethylphosphonium Bromide.—An ether solution of 0.0027 mole of sodium triphenylmethyl was added to 1.2 g. (0.002 mole) of the phosphonium salt. After shaking for a few minutes the solution lost its color and a red precipitate of the phosphinemethylene appeared. After one day the reaction flask was opened and the reaction mixture was filtered. From the precipitate triphenylphosphinediphenylmethylene melting at 171–173° was obtained. From the ether solution triphenylmethane (m. p. 91–92°) was isolated. Its identity was established by a mixed melting-point determination with known triphenylmethane.

Sodium Triphenylmethyl and Triphenyl-isopropylphosphonium Bromide.—An ether solution of 0.003 mole of sodium triphenylmethyl was added to 1.2 g. of triphenyl-*iso*-propylphosphonium iodide. The reaction mixture was allowed to stand for about forty-eight hours. During this time the color of the solution changed slightly and no longer was that of the original solution. When the reaction mixture was opened to the air the color was almost instantly discharged. The insoluble salts were removed by filtration. The filtrate was evaporated, the residue was dissolved in benzene and to the concentrated solution was added some petroleum ether (b. p. 40–60°). This gave a precipitate which after recrystallization from benzene and petroleum ether melted at 142–143°. Analysis of the product showed it to be diphenyl-isopropylphosphine oxide.

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[12] Dodanow and Medox, *Ber.*, **61B**, 907 (1928).

[13] Michaelis and Soden, Ann., 229, 295 (1885).

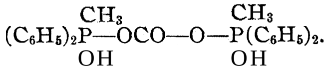
Anal. Subs., 0.1144: CO_2, 0.3092; H_2O, 0.0734. Calcd. for $C_{21}H_{22}PO$: C, 73.77; H, 6.97. Found: C, 73.71; H, 7.12.

From the benzene–petroleum ether mother liquors, triphenylmethane (m. p. 91–92°) was isolated.

Sodium Triphenylmethyl and Triphenylmethylphosphonium Iodide.—An ether solution containing 0 01 mole of sodium triphenylmethyl was added to 4 g. (0.01 mole) of triphenylmethylphosphonium iodide. The deep red color of the solution was discharged and at the end of three weeks a light orange colored solution remained. On exposure to the air, this color disappeared almost entirely. Moist carbon dioxide was passed into the solution and a white precipitate separated. The precipitate was removed by filtration. From the filtrate triphenylmethane (m. p. 91.5–92°) was obtained.

The precipitate produced by the carbon dioxide was purified by solution in chloroform, followed by precipitation with dry ether. In this way a compound melting at 109–111° with evolution of gas was obtained. This compound was very soluble in alcohol. When treated with acids it liberated carbon dioxide.

Anal. Subs., 0.2442: CO_2, 0.5886; H_2O, 0.1291. Calcd. for $C_{27}H_{28}P_2O_5$: C, 65.59; H, 5.67. Found: C, 65.74; H, 5.86.

The properties and analysis of this compound indicated that it was the basic carbonate of diphenylmethylphosphine oxide,  $(C_6H_5)_2\overset{CH_3}{\underset{OH}{P}}—OCO—O—\overset{CH_3}{\underset{OH}{P}}(C_6H_5)_2$.

Lithium *n*-Butyl and Triphenylethylphosphonium Iodide.—A petroleum ether solution containing 0.025 mole of lithium n-butyl was added to 10 g. (0.024 mole) of triphenylethylphosphonium iodide. In a short time the solution took on an orange color. After the reaction flask had stood for four days it was opened and water vapor was admitted. The color disappeared at once. Most of the petroleum ether was evaporated and the residue was extracted with benzene. Some unreacted phosphonium salt and the lithium iodide were undissolved. Addition of petroleum ether to the benzene solution precipitated an oil which slowly crystallized. This product was recrystallized from alcohol and water and again from benzene and petroleum ether. It then melted at 118–119.5°. It was shown to be ethyldiphenylphosphine oxide since the melting point (119–120°) was unchanged when mixed with an authentic specimen of this compound.

When sodium triphenylmethyl was used with triphenylethylphosphonium iodide, there was some difficulty in isolating a pure phosphine oxide.

Sodium Triphenylmethyl and Tetra-ethylphosphonium Iodide.—Preliminary experiments demonstrated that sodium triphenylmethyl solutions in ether reacted with tetraethylphosphonium iodide to give colorless products. Dry carbon dioxide had no effect on the reaction mixture. Water in contact with the ether solutions was neutral, showing that no basic oxide was present.

An ether solution of 0.01 mole of sodium triphenylmethyl was added to 2.7 g. (0.01 mole) of tetra-ethylphosphonium iodide. On opening the reaction flask a strong odor of triethylphosphine was noted. To a portion of the filtered ether solution was added an aqueous solution of zinc iodide in an attempt to isolate the double salt which Hofmann[14] reports as having a melting point of 99°. A small quantity of a solid melting at 82–88° was obtained. A second portion of the ether solution was treated with ethyl iodide and the quaternary phosphonium salt separated. This melted at 270–278°. Triphenylmethane (m. p. 91–92") was isolated from another portion of the ether solution. Attempts to identify the ethylene which must also have been produced were not successful.

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[14] Hofmann, Ann. *Supl.*, 1, 1 (1861).

Summary

1. Alkali metal alkyls react with quaternary phosphonium halides at room temperature.

2. Tetra-ethylphosphonium iodide and sodium triphenylmethyl give at once colorless products and the reaction is apparently analogous to that between alkali metal alkyls and quaternary ammonium salts.

3. Triphenylalkylphosphonium halides react with alkali metal alkyls to give colored products, apparently identical with the phosphinemethylenes of Staudinger, as the primary products of the reaction. The products isolated from several different reactions of this type are easily explained as decomposition products of the intermediate phosphinemethylenes.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN SULFOCHLORIDES AND ORGANOMAGNESIUM HALIDES

BY HENRY GILMAN AND ROBERT E. FOTHERGILL

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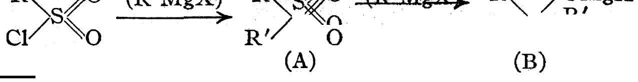
Introduction

In connection with studies on the electronic interpretation of the ethylenic linkage, Gilman and Peterson[1] reported a complete reaction between ethylmagnesium bromide and di-*p*-tolyldisulfonethylene. In order to throw some light on the nature of that reaction it was advisable to study a simpler conjugated system of the same type, namely, styryl-*p*-tolylsulfone (p-$CH_3C_6H_4\underset{O\quad O}{\underset{\diagup\diagdown}{S}}—CH=CHC_6H_5$). With this in view, we set out to prepare the sulfone from p-toluenesulfochlorideand styrylmagnesium bromide. The indifferent success attending this synthesis prompted a more general investigation of the reaction between sulfochlorides and RMgX compounds.

Earlier studies of this reaction were made by Hepworth and Clapham[2] and by Wedekind and Schenk.[3] Hepworth and Clapham[2] proposed the following reactions to account for the sulfones ($R—\underset{O\quad O}{\underset{\diagup\diagdown}{S}}—R$), sulfoxides ($R—\overset{O}{\overset{\diagup\!\!\diagup}{S}}—R$) and sulfides (R—S—R) isolated by them from the reaction between benzenesulfochloride and some RMgX compounds.


(I)

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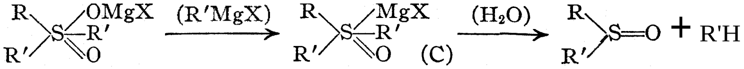
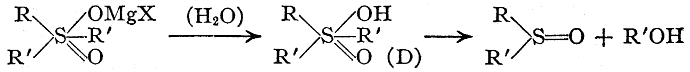
[1] Gilman and Peterson, THIS JOURNAL, 48, **423** (1926).

[2] Hepworth and Clapham, J. *Chem. Soc.*, 119, 1188 (1921).

[3] Wedekind and Schenk, *Ber.*, 54, 1604 (1921).

Compound B may then react further with R'MgX, as follows

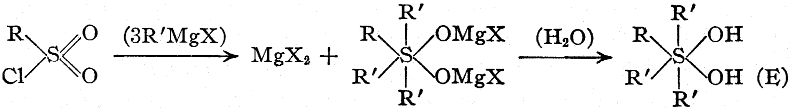

(II)


(III)

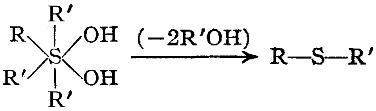
They explained the formation of sulfides by the further action of organomagnesium halide on Compounds B and C.

There are several objections to these reactions. First, an R'Cl compound is formed, the R' coming from the R'MgX and the Cl from the sulfochloride. Apparently they did not observe the formation of the chloride. Second, it is very doubtful if the intermediate compounds B, C and D are formed. Were such compounds formed, then it is reasonable to suppose that from Compound C, for example, one should get a mixture of sulfoxides, $R-\underset{\underset{O}{\|}}{S}-R'$ and $R'-\underset{\underset{O}{\|}}{S}-R'$. Actually, such mixtures of sulfoxides have not been reported. Third, the removal of oxygen when Compound B is converted to Compound C by means of an excess of R'MgX compound involves the oxidation of the R'MgX to an alcohol or a phenol; but, as stated by them in connection with their Reaction III, alcohols and phenols were not observed. It is, of course, possible that the atom of oxygen might be removed by two additional molecules of RMgX to give R·R and $(MgX)_2O$. This, however, has the objection of requiring a larger quantity of R·R than that actually found.

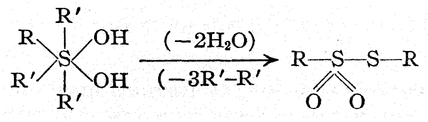
Wedekind and Schenk[3] proposed the following reactions to account for the same compounds isolated by Hepworth and Clapham,[2] in addition to the thiosulfonic ester, $R-\underset{O\;\;O}{S}-S-R$, they obtained.


(IV)

The formation of sulfide was explained by the removal of two molecules of R'OH, as follows

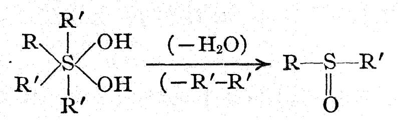

(V)

They explained the formation of the thiosulfonic ester by the removal of two molecules of water and three molecules of an R'–R' compound from two molecules of Compound E, as follows:



$$2\,\mathrm{RR'_3S(OH)_2} \xrightarrow[(-3\mathrm{R'}\text{-}\mathrm{R'})]{(-2\mathrm{H_2O})} \mathrm{R{-}\underset{O\ \ O}{S}{-}S{-}R}$$ (VI)

Finally, they proposed the following reaction for the formation of sulfoxide



$$\mathrm{RR'_3S(OH)_2} \xrightarrow[(-\mathrm{R'}\text{-}\mathrm{R'})]{(-\mathrm{H_2O})} \mathrm{R{-}\underset{\overset{\|}{O}}{S}{-}R'}$$ (VII)

There are also several objections to these reactions proposed by Wedekind and Schenk.[3] First, they make no mention of the formation of R'Cl compound. Second, the thiosulfonic esters are only what might be termed accidental reaction products; that is, the thiosulfonic esters only come into the picture of things after one of the true reaction products—the sulfinic acids, RSO_2H—are formed. It has long been known that sulfinic acids are readily converted to thiosulfonic esters.[4] Actually, we have shown that only sulfinic acid is obtained when the reaction products are worked up promptly, and that thiosulfonic esters and not sulfinic acids are obtained when the solutions containing sulfinic acids are allowed to stand for an appreciable time. Third, it seems reasonable to expect that Reaction V should give rise to a mixture of sulfides, namely, R—S—R' and R'—S—R'. Fourth, it seems equally reasonable to expect that Reaction VI should lead to a mixture of thiosulfonic esters, and Reaction VII to a mixture of sulfoxides, $\mathrm{R{-}\underset{\overset{\|}{O}}{S}{-}R'}$ and $\mathrm{R'{-}\underset{\overset{\|}{O}}{S}{-}R'}$. A fifth objection can be raised against Reactions VI and VII. Each of these reactions postulates the formation of R·R compounds. In our studies the quantities of diphenyl and of di-p-tolyl are only slightly greater than one would expect of these R·R compounds incidental to the preparation of phenylmagnesium bromide and p-tolylmagnesium bromide, respectively. Wedekind and Schenk[3] believed that Reactions VI and VII were reasonable because of the quantity of diphenyl they obtained. Actually, however, the yields of diphenyl reported by them are no greater than those generally obtained in a careful preparation of phenylmagnesium bromide.

As usual, it is generally an easier thing to criticize a series of reactions than to propose a series that can withstand criticism. The chief products isolated by us, and under our experimental conditions, were sulfones, sulfinic acids and RX compounds (the R coming from the Grignard reagent and the X from the sulfohalide). In the later more exact experiments, after we were aware of the formation of sulfinic acids and RX com-

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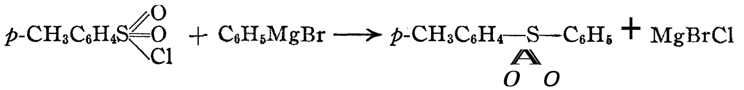
[4] **Gilman, Smith and Parker, This Journal, 47,** 851 (1925). **This paper, on the constitution of thiosulfonic esters, contains many of the important and leading references to the reactions of sulfinic acids, etc.**

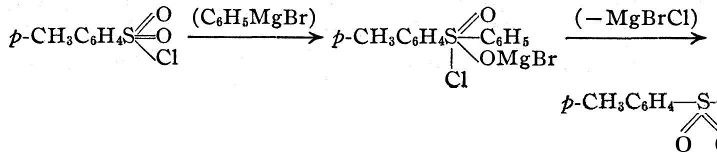
pounds, we observed that these two products were formed in about equivalent quantities.

The most reasonable reaction for the formation of sulfones is a so-called direct substitution, as follows



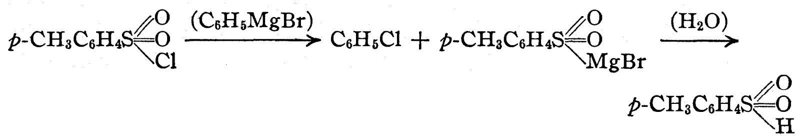
$$p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup\!\!\diagup O\\ = O\\ \diagdown Cl\end{smallmatrix} + C_6H_5MgBr \longrightarrow p\text{-}CH_3C_6H_4\text{—}\underset{O\quad O}{\underset{\diagup\!\!\diagup\,\diagdown\!\!\diagdown}{S}}\text{—}C_6H_5 + MgBrCl \qquad (VIII)$$

Of course, there is the possibility that these products might have resulted subsequent to addition of the Grignard reagent to the sulfonyl group (S=O), as follows



$$p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup\!\!\diagup O\\ = O\\ \diagdown Cl\end{smallmatrix} \xrightarrow{(C_6H_5MgBr)} p\text{-}CH_3C_6H_4\underset{Cl}{\underset{|}{S}}\begin{smallmatrix}\diagup\!\!\diagup O\\ \text{—}C_6H_5\\ \diagdown OMgBr\end{smallmatrix} \xrightarrow{(-MgBrCl)} p\text{-}CH_3C_6H_4\text{—}\underset{O\quad O}{\underset{\diagup\!\!\diagup\,\diagdown\!\!\diagdown}{S}}\text{—}C_6H_5 \qquad (IX)$$

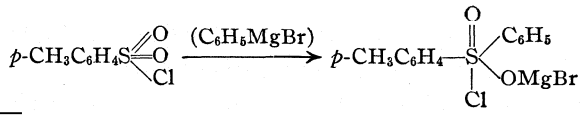
Probably the most acceptable reaction for the formation of sulfinic acid and halide is again a direct substitution (like that of Reaction VIII) but this time the halogen of the sulfohalide is replaced by the —MgX group and not by the R-group of the RMgX compound, as follows



$$p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup\!\!\diagup O\\ = O\\ \diagdown Cl\end{smallmatrix} \xrightarrow{(C_6H_5MgBr)} C_6H_5Cl + p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup\!\!\diagup O\\ = O\\ \diagdown MgBr\end{smallmatrix} \xrightarrow{(H_2O)} p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup\!\!\diagup O\\ = O\\ \diagdown H\end{smallmatrix} \qquad (X)$$

A direct substitution of the kind pictured in Reaction X finds support in reactions between the Grignard reagent and compounds having halogen attached directly to sulfur.[5]

There is an attractiveness to postulating addition of the RMgX compound to a sulfonyl group after the proposals of Hepworth and Clapham,[2] Wedekind and Schenk[3] and Reaction IX. However reasonable such a mode of reaction may appear for the explanation of reactions of sulfochlorides, sulfones and sulfoxides, it is of dubious value in interpreting the formation of sulfinic acid and RX compound. If a reaction of this type occurred



$$p\text{-}CH_3C_6H_4S\begin{smallmatrix}\diagup\!\!\diagup O\\ = O\\ \diagdown Cl\end{smallmatrix} \xrightarrow{(C_6H_5MgBr)} p\text{-}CH_3C_6H_4\text{—}\overset{O}{\underset{Cl}{\underset{|}{\overset{\|}{S}}}}\begin{smallmatrix}\diagup C_6H_5\\ \\ \diagdown OMgBr\end{smallmatrix} \qquad (XI)$$

(F)

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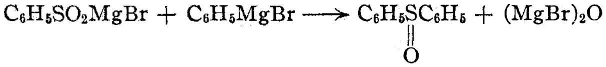
[5] Ferrario, Bull. *soc. chim.*, *7*, 518 (1910), obtained increasing quantities of chlorobenzene from the reaction between sulfur monochloride, dichloride and tetrachloride, respectively, with phenylmagnesium bromide. However, because we have not obtained chlorobenzene from sulfur monochloride, nor from aryl sulfur chlorides (RSCl), and because chlorobenzene is obtained from organic hypochlorites (ROCl) [see Durand and Naves, ibid., 37, 717 (1925); Gilman and Heckert, *Rec. trav. chim.*, *49*, *(1930)*] there is a possibility, even though somewhat remote, that sulfochlorides might have a hypochlorite structure, RS(=O)(OCl), in equilibrium with the RSO_2Cl form.

then it appears eminently reasonable that the splitting products should be mixtures of chlorobenzene and *p*-chlorotoluene, and benzenesulfinic acid and p-toluenesulfinic acid. Such mixtures were not observed, and the products isolated were cldorobenzene and p-toluenesulfinic acid. Furthermore, from benzenesulfochloride and *p*-tolylmagnesium bromide the products were benzenesulfinic acid and *p*-chlorotoluene. This pair of reactions, with the R groups interchanged in the sulfochloride and Grignard reagent, militates against a preliminary addition and indicates a direct substitution.[6]

Our experimental conditions were not those of earlier workers.[2,3] We used equivalent molecular proportions of sulfochloride and Grignard reagent and did not heat the reaction mixtures. However, when we did follow their general directions, we obtained some diphenyl sulfide, a large yield of diphenyl sulfoxide, an equally large yield of chlorobenzene but no sulfinic acid. The absence of sulfinic acid and the high yield of sulfoxide is very probably due to the following reaction[4]



$$C_6H_5SO_2MgBr + C_6H_5MgBr \longrightarrow C_6H_5\underset{\underset{O}{\|}}{S}C_6H_5 + (MgBr)_2O \qquad \text{(XII)}$$

Closely related to the present studies is earlier work by Oddo[7] on sulfuryl chloride (SO_2Cl_2) and by Oddo,[8] Grignard and Zorn,[9] and Strecker[10] on thionyl chloride ($SOCl_2$).

Experimental Part

The reactions were carried out in a three-necked flask provided with a mercury-sealed stirrer, separatory funnel and condenser. The flask containing generally 0.3 mole of sulfochloride in one liter of ether was cooled by an ice-salt mixture. To this was slowly added (three to four hours) the Grignard reagent, and when one molecular equivalent of RMgX compound was added the reaction mixture generally gave the color test described by Gilman, Schulze and Heck.[11] The cold reaction mixture was hydrolyzed with 10% hydrochloric acid, the ether layer separated and then combined with the ether washings of the acid-aqueous layer.

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[6] Of course, we would not be understood to mean that there is no preliminary addition here of a loose type not involving primary or chief valences of the sulfur or oxygen or chlorine or, for that matter, of the magnesium or ether in the Grignard reagent. What we do mean is that a hypothetical compound like Compound F is unreasonable if the phenyl and the *p*-tolyl groups are attached to the sulfur by primary valences. Also, admittedly, the sulfur–carbon linkages holding the phenyl and *p*-tolyl groups would not be, in all probability, of equal strength even though both such linkages were primary. Linkages of slightly different strengths should result, generally, in mixtures having slightly different percentages of components.

[7] Oddo, *Gazz. chim. ital.*, II, 35, 136 (1905); *Atti accad. Lincei* [5] *I*, 14, 169 (1905); see *Chem. Zentr.*, I, 1145 (1905).

[8] Oddo, *Gazz. chim. ital.*, *I*, 41, 11 (1911); C. A., 5,2635 (1911).

[9] Grignard and Zorn, *Compt. rend.*, 150, 1177 (1910).

[10] Strecker, *Ber.*, 43, 1131 (1916).

[11] Gilman and Schulze, THIS JOURNAL, 47, 2002 (1925); *Bull. soc. chim.*, 41, 1479 (1927); Gilman and Heck, *Rec. trav. chim.*, 48, 193 (1929); *Ber.*, **62,** 1379 (1929).

TABLE I

REACTION BETWEEN SULFOHALIDES AND GRIGNARD REAGENTS

Sulfohalide	Moles	RMgX compound[a]	Sulfone	Yield, %	Sulfinic acid[b] yield, %	RX compound	Yield, %
$C_6H_5SO_2Cl$	0.3	C_6H_5MgBr[c]	$C_6H_5SO_2C_6H_5$	35.0	0.5	C_6H_5Cl	16.3
$C_6H_5SO_2Cl$	.3	p-$CH_3C_6H_4MgBr$[d]	p-$CH_3C_6H_4SO_2C_6H_5$	17.5	46.4	p-$CH_3C_6H_4Cl$	27.0
$C_6H_5SO_2Cl$	.2	α-$C_{10}H_7MgBr$[e]	......	..	..	α-$C_{10}H_7Cl$	39.7
$C_6H_5SO_2Cl$	.3	$C_6H_5CH{=}CHMgBr$[f]	......	..	39.6	$C_6H_5CH{=}CHCl$	40.4
$C_6H_5SO_2Cl$	.3	$C_6H_5C{\equiv}CMgBr$[g]	......	..	1.2	$C_6H_5C{\equiv}CCl$	13.7
$C_6H_5SO_2Cl$	.3	$C_6H_5CH_2MgCl$[h]	$C_6H_5CH_2SO_2C_6H_5$	2.9	..	$C_6H_5CH_2Cl$	60.0
p-$CH_3C_6H_4SO_2Cl$	.3	n-C_4H_9MgBr[i]	......	..	60.6	n-C_4H_9Cl	8.7
p-$CH_3C_6H_4SO_2Cl$	.3	Cyclo-$C_6H_{11}MgBr$[j]	......	..	67.1	Cyclo-$C_6H_{11}Cl$	66.3
p-$CH_3C_6H_4SO_2Cl$	.3	C_6H_5MgBr[k]	p-$CH_3C_6H_4SO_2C_6H_5$	32.9	10.7	C_6H_5Cl	11.0
p-$CH_3C_6H_4SO_2Br$	.1	C_6H_5MgBr[l]	......	..	30.2	C_6H_5Br	53.8
p-$CH_3C_6H_4SO_2I$	.13	C_6H_5MgBr[m]	......	..	11.8	C_6H_5I	65.1
α-$C_{10}H_7SO_2Cl$	.2	C_6H_5MgBr[n]	α-$C_{10}H_7SO_2C_6H_5$	13.0	..	C_6H_5Cl	24.5

[a] Unless otherwise stated, the quantity of RMgX compound used was equivalent to the sulfohalide. That is, with 0.3 mole of sulfohalide, 0.3 mole of RMgX compound was used.

[b] The sulfinic acid obtained was that corresponding with the sulfohalide. For example, with benzenesulfochloride there was obtained benzenesulfinic acid. A search was not always made for the sulfinic acid.

[c] The reactions between benzenesulfochloride and phenylmagnesium bromide were the first studied, and the very small yields of sulfinic acid and chlorobenzene given in Table I were due to an initial unfamiliarity with the course of the reaction. Several experiments were made on the reaction between benzenesulfochloride and phenylmagnesium bromide, and although the yield of diphenylsulfone was consistently around 35%, the yield of chlorobenzene varied between 12.2 and 43.7%. A reaction between these reagents at a temperature below −63° (by solid carbon dioxide and acetone cooling) gave 12.2% of sulfone, 43.7% of chlorobenzene and 6.5% diphenyl, but the sulfinic acid was lost by an attempted vacuum distillation. We had little success in a low temperature reaction so carried out that a mixture of benzenesulfochloride and bromobenzene was added to magnesium and ether.

[d] In addition to the products listed there was obtained 5.2% of di-p-tolyl. No p-cresol was obtained.

[e] A few crystals melting at 97–100° were obtained. These, however, were not the expected α-naphthylphenylsulfone, because of the depression to 70–80° in a mixed melting point determination with an authentic specimen of the sulfone. Unfortunately the alkaline extract that might have contained the sulfinic acid was lost by a mishap.

[f] The yield of diphenylbutadiene from this experiment was **34.2%**. We believe that this high yield of R·R compound is due to the extensive coupling reaction incidental to the preparation of β-styrylmagnesium bromide. No sulfone was obtained and inasmuch as the sulfone that might have been expected here was the cause of this study a further investigation is in progress on this reaction. The recovery of a 33.6% yield of styrene (which very probably resulted from hydrolyzed Grignard reagent) is indicative of a lesser reactivity of this RMgX compound toward benzenesulfochloride.

[g] The recovery of phenylacetylene in a 51.2% yield is indicative of a very slow or poor reaction of phenylacetenylmagnesium bromide. This supports other studies now in progress on the relative reactivities of Grignard reagents. However, only 4.5% of the benzenesulfochloride was recovered.

[h] The yield of dibenzyl was **7.7%**. In a careful preparation of benzylmagnesium chloride the yield of dibenzyl is 4–5%.

[i] A residue, non-volatile with steam, was obtained. This melted at 68" when recrystallized twice from **95%** alcohol. The yield was 13.2 g, and analyses for sulfur by the Carius method gave **17.07** and 17.40% of sulfur. Gilman and Beaber, THIS JOURNAL, 47, **1449** (1925), reported *n*-butyl-*p*-tolylsulfone as a liquid boiling at **173–175" (3.5** mm.).

[j] A very small quantity **(0.2** g.) of a solid melting at 86° was obtained from the residue of the steam distillation.

[k] The yield of diphenyl was 4.5% of that normally obtained incidental to the preparation of phenylmagnesium bromide.

[l] The *p*-toluenesulfobromide and *p*-toluenesulfo-iodide were prepared according to the directions of Whitmore, THIS JOURNAL, 45, **1069 (1923).** The sulfobroinide was partially dissolved in **700** cc. of ether and **0.4** mole of phenylmagnesium bromide was required for a positive color test. The reaction flask was cooled by an ice-salt bath, and **20%** hydrochloric acid was used in the hydrolysis. The 30.2% yield of *p*-toluenesulfinic acid is based on the yield of *p*-tolyl-*p*-toluenethiosulfonate isolated in this experiment.

[m] The quantity of phenylmagnesium bromide required for a positive color test was **0.7** mole. The initially violent reaction may have been due to some free halogen. No *p*-toluenesulfinic acid was actually isolated and the yield of this compound was based on the *p*-tolyl-*p*-toluenethiosulfonate (see Footnote *l*.)

[n] As in other experiments with phenylmagnesium bromide, the yield of diphenyl was that to be expected from the preparation of phenylmagnesium bromide.

The ether layer, after washing with 5% sodium hydroxide and then with a little water, was steam distilled. The steam distillate was extracted with ether and from the vacuum distillation of this dried ether extract there was obtained the RX and R–R compounds. The residue from steam distillation gave the sulfone.

The alkaline extract was immediately acidified with hydrochloric acid and extracted with ether. This ether solution was then dried by sodium sulfate, and on the rapid removal of the ether by dry air the sulfinic acid was obtained as faintly colored crystals.

The identity of all of the solid reaction products was confirmed by mixed melting point determinations with authentic specimens. The liquid RX compounds were identified by conversion to solid nitro-halogen derivatives, and mixed melting point determinations were then made of these solids with authentic compounds. The results are given in Table I and the footnotes which accompany it.

Benzenesulfochloride and **Phenylmagnesium** Bromide.—This experiment was carried out under conditions unlike those followed in the runs described in Table **I**, but like those described by Hepworth and Clapham[2] During the addition of **53** 0 g. **(0.3** mole) of benzenesulfochloride in **200** cc. of ether to **0.9** mole of phenylmagnesium bromide solution (450 cc.), the reaction flask was cooled by an ice–salt mixture When addition was ended, the mixture was allowed to stand at room temperature for seventeen hours and then warmed by a hot plate for one hour. After hydrolysis by dilute hydrochloric acid, the mixture was worked up in the customary manner The following products were obtained: 52.5% of chlorobenzene, 60.2% of diphenyl sulfoxide, 4.1% of diphenyl sulfide, 6.4% of diphenyl, but no benzenesulfinic acid.

Summary

The chief products obtained from the reaction between arylsulfohalides and organomagnesium halides are sulfones, sulfinic acids and RX compounds having the R-group of the RMgX compound and the halogen of the sulfohalide. Previous explanations of this reaction have been corrected and a new interpretation of the reaction has been proposed.

AMES, IOWA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE STANDARD OIL COMPANY OP INDIANA]

TETRAMETHYLETHYLENE SULFIDE

BY MERRILL A. YOUTZ AND PHILIP P. PERKINS

RECEIVED JULY 11, 1929 PUBLISHED NOVEMBER 8, 1929

It is only in comparatively recent years that substances of the type of ethylene sulfide $\overline{\mathrm{CH_2SC}}\mathrm{H_2}$ have been synthesized. Previous attempts to do so by treating alkylene dibromides with potassium sulfide, etc., have given either a dimer, such as diethylene disulfide or amorphous substances of even higher molecular weights. This is not especially surprising and probably in some cases long chains could be produced by the reaction of each mole of potassium sulfide with two different molecules of $C_2H_4Br_2$. However, the matter is even more involved than this as the recent successful preparation of several of these compounds by Delépine[1] has shown that, even if pure, they polymerize readily. The tendency to polymerize diminishes with increasing molecular weight. His method was to treat a 1,2-dibromide with potassium or ammonium thiocyanate, purify the dithiocyanate and to treat this with dilute sodium sulfide. Especially with the lowest member it was necessary to have the sodium hydrogen sulfide present with the sodium sulfide in order to avoid polymerization during the reaction.

The compounds are readily polymerized by bases or acetic or sulfuric acids. Nitric acid oxidizes them to sulfuric or sulfonic acids. Hydrochloric acid appears to combine forming a chloromercaptan which can be removed with sodium plumbite, etc. Probably the oxidation by nitric

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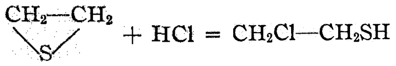
[1] Delépine, *Compt. rend.*, **171**, **36** (1920); **172**, 158 (1921); Bull. *soc. chim.*, [4] **27**, 740 (1920); **29**, 136 (1921).

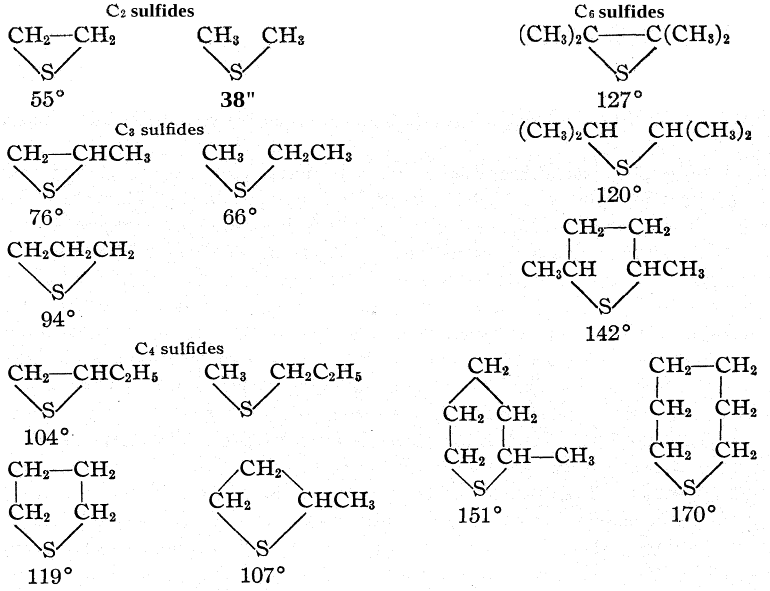
acid, which takes the same course as with a mercaptan, is preceded by this mercaptan formation



They form addition compounds with heavy metal salts and methyl iodide. The boiling points are a little higher than those of the corresponding alkyl sulfides but lower than those of the isomers having a larger ring.

TABLE I

SULFIDES AND THEIR BOILING POINTS



The tetramethylethylene sulfide here described resembles the simpler members in its chemical properties though it is more stable. It was prepared by the reactions

$$\text{Acetone} \xrightarrow{\text{H}} \text{Pinacone hydrate} \xrightarrow{70\%\ \text{HBr}} \text{Teramethylethylene dibromide} \xrightarrow{\text{KSCN}} \text{Dithiocyanate} \xrightarrow{Na_2S} \text{Sulfide}$$

As might be expected from its symmetry, it is a solid, m. p. 76°, b. p. 127°, and has great powers of crystallization. The crystals are usually needle-like if sublimed, but if allowed to sublime at room temperature by standing in a container, it forms perfect cubic crystals of diamond-like brilliancy. On one occasion the whole of a preparation crystallized overnight from a petroleum ether solution in a single crystal over two inches long and weighing about ten grams. It has an extremely powerful odor, not exceedingly unpleasant and resembling that of camphor. It is very soluble in all the usual organic solvents though not in water. It cannot be recrystallized satisfactorily at elevated temperatures because of its volatility. It can be recrystallized from low-boiling (25–40°) petroleum ether by evaporating off part of the solvent with an air stream at a low temperature and then chilling to −15 or −20° and filtering on a cold filter. It can also be purified by sublimation.

It is easily polymerized to amorphous insoluble particles by concentrated sulfuric acid even in dilute naphtha solution, from which it is very completely removed. It forms addition compounds with mercuric chloride and with silver nitrate in absolute or 95% alcohol solution. It reacts only slightly with methyl iodide.

Experimental Part

Pinacone Hydrate.—This was made from acetone by reduction with magnesium amalgam.[2]

Tetramethylethylene **Dibromide.**—This was made according to the procedure of Thiele[3] by treating pinacone hydrate with 70% hydrobromic acid; yields, 50–85%. The use of spent acid resaturated with hydrogen bromide gave progressively lower yields. Apparently a liquid substance accumulates in solution in the acid. It is a severe lachrymator and is probably the bromohydrin, which is the chief product if insufficient or too weak acid is used. The crude product was dried and recrystallized from glacial acetic acid and used soon after.

Tetramethylethylene **Dithiocyanate.**—Fifty cc. of methyl alcohol and 19.4 g. of potassium thiocyanate (or 15.2 g. of ammonium thiocyanate, 4 moles) were refluxed for a few minutes; 12.2 g. of dibromide was added and the mixture first warmed and shaken, and then refluxed for ten to fifteen minutes; 250 cc. of water was added and the mixture extracted four times with 100-cc. portions of light petroleum ether while still slightly warm. The dithiocyanate is very insoluble in cold naphtha and only slightly soluble in warm naphtha. The naphtha was nearly all evaporated by air blowing on the steam-bath; the remainder was cooled in ice and the hard grainy precipitate filtered with suction. The yield was 4.5–5.5 g. (45–55%). Less potassium thiocyanate reduces the yield, while more increases it only slightly. The dibromide should be freshly recrystallized, dry and free from acetic acid. The dithiocyanate, recrystallized from alcohol, melts at 61°.

Anal. Calcd.: N, 14.0; S, 32.0. Found: N, 14.4, 14.5; S, 31.4, 31.7.

Tetramethylethylene Sulfide.—Twenty grams of dithiocyanate and 50 cc. of methyl alcohol were mixed in a flask provided with a reflux condenser. A solution of 25 g. of $Na_2S{\cdot}9H_2O$ (calcd., 24 g.) in 50 cc. of water was added. A slight warming occurred and the mixture was heated gently (not boiled) with shaking for thirty minutes and then cooled; 50 cc. of very light petroleum ether (b. p. 20–35° or 25–35°) was poured through the condenser to dissolve out sublimed sulfide, then the mixture was placed in a separatory funnel, water added, the mixture shaken and the layers separated. The lower layer was washed again with 50 cc. of the petroleum ether. These extracts were evaporated by an air stream while keeping very cold, until nearly all the solvent was gone (6–8 cc.). The evaporation must not be prolonged as the sulfide is very volatile.

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[2] Marvel, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, pp. 87–89.

[3] Thiele, Ber., 27, 455 (1894).

The solution was chilled in a freezing mixture, the crystals filtered with slight suction on a cold Biichner funnel with paper and the filtrate added to the next preparation; yield, 90–95%. It may contain dithiocyanate, from which it can be freed by sublimation; m. p. 76.1–76.6°; b. p. 127" (corr.) (by the Siwolliboff capillary tube method); sulfur, 27.5%; calcd., 27.6%. The molecular weight of the crude sulfide was determined by the freezing-point method in benzene: (1) 16.00 g. of solvent; 0.1423 *g*. of sample, depression 0.385°, molecular weight 115.5; (2) 0.2672 g. of sample, depression 0.719°, molecular weight 116.1, calcd. 116.19. Hence it contained no polymers.

Summary

Tetramethylethylene sulfide was prepared by the series of reactions acetone → pinacone hydrate → tetramethylethylene dibromide → dithiocyanate → sulfide, and some of its properties have been recorded.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE STANDARD OIL COMPANY, INDIANA]

TRIMETHYL- AND TRIMETHYLETHYLTHIOPHENE

BY MERRILL A. YOUTZ AND PHILIP P. PERKINS

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Perhaps the most obvious method of preparing polyalkylthiophenes of known structure is by means of the reaction of phosphorus pentasulfide or phosphorus trisulfide on 1,4-dicarbonyl compounds. If the a-positions of the thiophene are to be substituted with alkyl groups, the carbonyl compound must be a diketone. The preparation of such compounds has proved to be extremely difficult. The only member thus far reported is 3,4-dimethylacetonylacetone prepared by Ciamician and Silber[1] by the action of light on methyl ethyl ketone and by Vladesco[2] by the action of sodium on methyl chloro-ethyl ketone. Willstatter and Clark[3] reported a large amount of work on attempts to produce such a diketone. While the action of iodine on sodium acetoacetic ester readily yields diacetylsuccinic ester, which is hydrolyzable to acetonylacetone with good yields, the attempt to carry out an analogous reaction with ethyl sodium acetoacetic ester has uniformly failed. Also the attempt to introduce alkyl groups into sodium diacetylsuccinic ester leads chiefly to ethers, and such of the desired compound as is produced readily loses one or more acetyl groups by hydrolysis or alcoholysis.[3] We have found that another variation of this synthesis gives negative results: the action of sodium on a-bromo-a-ethyl acetoacetic ester. An attempt to repeat the work of Vladesco where sodium is allowed to react with methyl chloro-ethyl ketone yielded no detectable amount of the desired diketone. Also the ethyl

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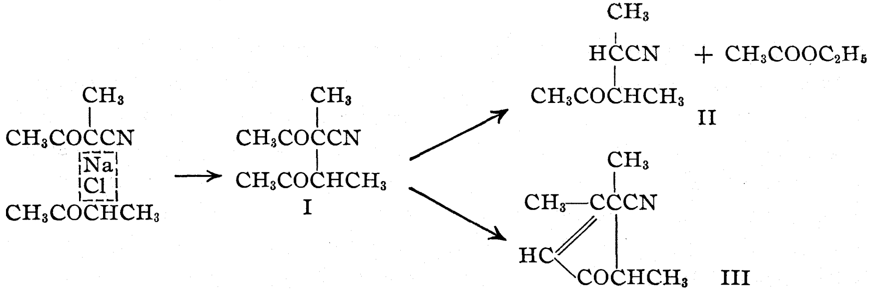
[1] Ciamician and Silber, *Ber.*, 45, 1540 (1912).

[2] Vladesco, Bull. *soc. chim.*, **[3]** ***6***, 809 (1891).

[3] Willstätter and Clark, ***Ber.***, 47, 291–310 (1914).

acetal of this ketone appeared to react with sodium but did not give the diketone acetal or the diketone.

The nitrile $CH_3COCHCNCH_3$,[4,5] prepared from methyl chloroethyl ketone and potassium cyanide, was converted into its sodium compound and this allowed to react with the chloroketone. The reaction yielded, besides unchanged nitrile, a substance b. p. 171° (760 mm.); b. p. 75° (25 mm.); d_4^{20} 0.957 (the first nitrile boils at 145°). It was colorless and had a strong odor. From its low boiling point it could hardly have been the expected diacetonitrile (I) but was perhaps the nitrile of α,β-dimethyl-levulinic acid (II) formed by the alcoholysis of one acetyl group from I, or perhaps a cyclic ketone-nitrile (III) formed from I by internal condensation. The ethyl ester of the acid corresponding to the nitrile (I) was shown to behave in this manner; but III would probably have had a higher boiling point than we observed since the corresponding ethyl ester according to Willstatter had a boiling point of 125–135° at 11 mm., and in general a nitrile of an acid has a boiling point very near that of the ethyl ester of that acid.



The attempt to prepare a ketone from which a tetra-alkyl thiophene could be prepared directly was then abandoned. α,β-Diacetyl butyric ester (IV) was then prepared from sodium acetoacetic ester and methyl chloro-ethyl ketone by means of a slight modification of the method of

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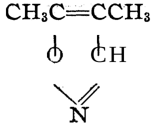
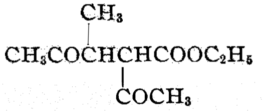
[4] Von Reymenant, *Bull. acad. roy. Belg.*, 724–742 (1900); *Chem. Centr.*, I, 95–96 (1901).

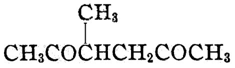
[5] There is doubt in the minds of the authors that the substance produced in the manner described is really a nitrile. If it is, it would be the nitrile of methylacetoacetic acid and should have a boiling point of 180–190° instead of 145° as it has. Its elementary composition is that represented by the formula. From its anomalous boiling point, its basic properties, the formation of addition compounds with mercuric chloride and with methyl iodide and its very slow reaction with sodium, it seems much more probable that it is the isomeric 4,5-dimethyl isoxazole, as shown. If so, a whole series of isoxazoles can readily be prepared in a similar manner with high yields. However, such an isoxazole would probably behave toward sodium or sodium ethylate as if it were the nitrile, forming the expected sodium derivative of methyl acetoacetonitrile and hence be suitable for the work here described. The authors wish to reserve this field for further work.



Willstatter and Clark. This ester was hydrolyzed by boiling for several hours with an excess of 20% potassium carbonate solution to the new diketone, 3-methylacetonylacetone (V).


$\mathrm{CH_3CO\overset{\displaystyle CH_3}{\overset{|}{C}}H\underset{\underset{\displaystyle COCH_3}{|}}{C}HCOOC_2H_5}$

IV


$\mathrm{CH_3CO\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2COCH_3}$

V

This ketone reacted readily with phosphorus pentasulfide in the cold, giving after purification 2,3,5-trimethylthiophene.

2,3,4-Trimethylthiophene, the only position isomer possible, has been prepared by Victor Meyer.[6] Our thiophene with isatin and sulfuric acid gives a brilliant brownish-red color but not blue or green. 2,5-Dimethylthiophene, where both a-positions also are substituted, does likewise[7] but the 2,3,4-compound gives a green color.

Our thiophene reacted readily with acetyl chloride and aluminum chloride giving 2,3,5-trimethyl-4-acetothienone. This ketone has an unpleasant penetrating odor similar to but much stronger than that of the thiophene itself. The ketone was reduced by the method of Clemmensen, giving 2,3,5-trimethyl-4-ethylthiophene.

This thiophene does not give the indophenine reaction. Both thiophenes dissolve in concentrated sulfuric acid with slight discoloration and a slight heat evolution. Both are reprecipitated on dilution though probably the trimethylthiophene is converted to a sulfonic acid to some extent. This inertness is in great contrast to the ready reaction of thiophene itself with sulfuric acid. Both thiophenes show the characteristic depression of the molecular refraction, while the trimethylacetothienone has *a* normal value.

The trimethylthiophene reacts readily with iodine in the presence of yellow mercuric oxide to give an iodo compound. This was only distillable in steam and was probably impure.

Experimental Part

Diethyldiacetosuccinic Ester.—α-Bromo-α-ethylacetoacetic ester was prepared according to the method of Macbeth.[8] The boiling point, however, is 100–102° at 11 mm. and not 106°. Four and two-tenths grams of sodium (calcd. 3.8 g.) was placed in 150 cc. of dry ether and 26.3 g. of ethylacetoacetic ester added and allowed to reflux for two hours with shaking. The solution was poured off the remaining sodium and mixed with 39.5 g. of a-bromo-a-ethylacetoacetic ester. The solution became warm, and sodium bromide precipitated in one to two minutes, after which the solution was refluxed for ten minutes. It stood for sixteen hours and although still slightly alkaline was treated with water, washed and dried with sodium sulfate. After evaporation of

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[6] Victor Meyer, "Die Thiophengruppe," Braunschweig, 1888, pp. 59–60.

[7] Ref. 6, p. 53.

[8] Macbeth, J. *Chem.* Soc., 123, 1127 (1923).

ether, there remained 36 g. of a brown oil which did not crystallize. It gave no diketone (3,4-diethylacetonylacetone) when boiled with potassium carbonate solution.

3,4-Dimethylacetone.—Methyl α-chloro-ethyl ketone was prepared by passing chlorine into a stirred mixture of two parts of methyl ethyl ketone, two parts of water and one part of powdered calcium carbonate under a reflux and at 60–70° until the calcium carbonate was gone. Sodium was put in 200 cc. of dry ether and 128 g. (3 moles) of chloro ketone added. The mixture boiled spontaneously at first and was then heated until the reaction was complete (about one hour). The solution was filtered, washed, dried and fractionated. No diketone whatever was obtained, the product being unchanged chloro ketone and very high boiling products. Another trial, in which the sodium (as wire) was added during the course of the reaction, gave no better results. Heating of the chloro ketone with Kahlbaum's copper powder in a sealed tube at 150–160° gave no reaction. At 170–180° some decomposition occurred but no diketone was obtained.

Methyl chloro-ethyl ketone diethyl acetal was prepared by the method of Claisen[9] from 75 g. (3 moles) of absolute ethyl alcohol, 66.8 g. of chloro ketone and 102 g. of ethyl ortho-formate; yield, 70% in ten days' standing. The acetal showed b. p. 80–84° (36 mm.); d_4^{20} 0.9773; Cl, 19.3%; calcd. 19.6%. Without ammonium chloride as a catalyzer the yield was 39%. A shorter time of standing (four days) gave a 45% yield. Probably a longer period would increase the yield. Thirteen and seven-tenths grams of sodium wire (calcd. 11.7 g.) was placed in 300 cc. of dry ether with 93 g. of chloro acetal under a reflux condenser bearing a calcium chloride tube. The mixture was refluxed daily for five days, when the sodium was much disintegrated. The liquid was filtered, the residue washed once with dry ether and the combined filtrates were distilled, finally at reduced pressure; 32 g. of very pure acetal was recovered but no other products except ether.

3-Methylacetonylacetone.—α,β-Diacetylbutyric ester was prepared as described by Willstatter and Clark[8] except that a 100% excess of acetoacetic ester was used. This doubled the yield. We obtained 45–60% yields with 60–80% recovery of the excess acetoacetic ester.

Two hundred and six grams of ester was refluxed for six hours with a solution of 200 g. of potassium carbonate in 800 cc. of water. The mixture was diluted with ether, the upper layer separated and the water layer extracted with ether. The combined extracts were dried with potassium carbonate and after removal of ether in a bead column, fractionated at reduced pressure; yield 109 g. **(83%);** b. p. 68–74°; properties: b. p. 71° (10 mm.); d_4^{20} 0.9527; n_D^{20} 1.4260; b. p. (740 mm.) 195–196° (corr.) with some decomposition. It is soluble in all the usual organic solvents and miscible with water in all proportions. As prepared above it had a rather strong odor but after purification with sodium bisulfite (by shaking with saturated sodium bisulfite solution, extracting with ether, and heating the sodium bisulfite solution with sodium carbonate) it had a sweet and pleasant odor. In other respects the purified and unpurified ketones had practically identical properties.

The semicarbazone (di-semicarbazone), when crystallized from hot water, melted at 219–220° corr.

Anal. Subs., 0.0848: 23.5 cc. of N at 0° and 760 mm. Calcd.: N, 34.7. Found: N, 34.7.

The *p*-nitrophenylhydrazone (or possibly the 2,3,5-trimethyl-N-*p*-nitrophenyliminopyrrole) was recrystallized from toluene; m. p. 112–113° corr.

2,3,5-Trimethylthiophene.—Sixty-five to 70 g. of powdered phosphorus pentasul-

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[9] Claisen, *Ber.*, 40, 3908 (1907).

fide in a flask with a reflux condenser was treated with 96 g. of 3-methylacetonylacetone, the mixture kept cool and not shaken for a few minutes (to avoid a too violent reaction), and then allowed to come to room temperature. Finally, it was heated to boiling for three to four hours with the addition of 10 g. of phosphorus pentasulfide after the first hour. The liquid was poured off the tarry residue, distilled, the distillate dried, refluxed over several portions of sodium and then sodium hydroxide, and fractionated. The yield was 35–40% of a colorless liquid with a durene-like odor; b. p. 163–165° corr. at 746 mm.; d_4^{20} 0.9753; n_D^{20} 1.5131; M_D^{20} 38.88, calcd. 39.50; sulfur calcd. 26.4, found 26.4. The sulfur was determined by analysis of a solution in naphtha by the Burton lamp method.

2,3,5-Trimethyl-4-acetothienone.—To 12 g. of powdered aluminum chloride in 50 g. of cold carbon disulfide in a flask with a reflux condenser was added a mixture of 10 g. of trimethylthiophene, 8 g. of acetyl chloride and 50 g. of carbon disulfide drop by drop during fifteen minutes. The mixture was allowed to stand for three to four hours in ice and water, then overnight at room temperature. The mixture was warmed for a few minutes, then cooled, decomposed with dilute sulfuric acid, diluted with ether, separated and the ether solution washed with dilute sulfuric acid, water, sodium carbonate and water; it then was dried and fractionated. The yield was 12.5 g. (93%); b. p. 245–250° corr. Other preparations gave 85–94% yields. The pure ketone boiled at 248–249" corr. (748 mm.); d_4^{20} 1.0891; n_D^{20} 1.5454; M_D^{20} 48.86, calcd. 48.75. *Anal.* (Parr oxygen bomb). Calcd.: S, 19.05. Found: S, 18.9. It formed no bisulfite compound.

The semicarbazone, when recrystallized from acetone, melted at 157° corr.

The p-nitrophenylhydrazone was recrystallized from xylene; m. p. 162.5–163° corr. *Anal.* Subs., 0.2102: 24.0 cc. of nitrogen at 0° and 760 mm. Calcd.: N, 13.9. Found: N, 14.2.

The phenylhydrazone was an oil which did not crystallize.

2,3,5-Trimethyl-4-ethylthiophene.—The acetothienone was reduced by the method of Clemmensen,[10] using 80 g. of zinc to 400 cc. of 5% mercuric chloride solution, pouring off this solution after one hour, adding the ketone (21.7 g.) and then 40 cc. of 6 N hydrochloric acid and refluxing, with further additions of 40 cc. of hydrochloric acid every one to two hours for fourteen hours. The yield was 70–80% after deducting unchanged ketone (15–25% of the original ketone). This thiophene boiled at 204–206° corr. at 748 mm.; d_4^{20} 0.9609; n_D^{20} 1.5132; M_D^{20} 48.25, calcd. 48.75. *Anal.* Calcd.: S, 20.78. Found: S, 20.8. These thiophenes gave the characteristic depression of the molecular refraction: trimethylthiophene, M_D^{20} 38.88, calcd. 39.50; trimethylethylthiophene, M_D^{20} 48.25, calcd. 48.75; trimethylacetothienone M_D^{20} 48.86, calcd. 48.75. This latter is probably to be interpreted as a depression, since an acetyl group on an aromatic nucleus usually produces an exaltation of 0.5 to 1.0 unit.[11]

Some attempts were made to prepare the compound by preparing iodotrimethylthiophene and treating it with sodium and ethyl bromide, but these were unsuccessful. Trimethylthiophene reacts readily with iodine and yellow mercuric oxide to give an iodo compound (which could not be distilled except with steam) but this gave no considerable amount of the desired product when treated with sodium and ethyl bromide. However, tetramethylthiophene has been made in this way.[12] Perhaps the success of the latter preparation depended on the fact that the group entered the α-position instead of the β-position as in our case. The α-positions are much more reactive.

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[10] Clemmensen, *Ber.*, 46, 1837 (1913); **47,** 51, 681 (1914).

[11] Brühl, *ibid.*, 40, 1159 (1907); Auwers and Eisenlohr, *ibid.*, 43, 806 (1910); Auwers and Kohlhaas, *J. prakt. Chem.*, **108,** 321–331 (1924).

[12] Zelinsky, *Ber.*, 21, 1837 (1888).

Summary

Attempts to synthesize a 3,4-dialkylacetonylacetone have yielded negative results, but 3-methylacetonylacetone was prepared and from it 2,3,5-trimethylthiophene by the action of phosphorus pentasulfide. From this thiophene was prepared 2,3,5-trimethyl-4-acetothienone, which was reduced to 2,3,5-trimethyl-4-ethylthiophene.

WHITING, INDIANA

NEW BOOK

Dispersoidanalyse. Die Methoden der Teilchengrössenbestimmung und ihre theoretischen Griindlagen. (The Methods for the Determination of the Size of Colloidal Particles and the Theoretical Considerations Involved.) BY FRIEDRICH-VINCENZ v. HAHN, Hamburg. Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1928. xxiv + 553 pp. 165 figs. 15.5 × 23.5 cm. Price, unbound, M. 39; bound, M. 42.

This monograph is Volume III of a handbook describing single aspects of colloid science. It deals with a problem which practical men in many fields, as, for example, those interested in the study of soil or clay, or filter-passing bacteria, have to solve. The book provides an admirable summary of our present resources in this direction. It describes the various experimental methods hitherto developed: optical, mechanical (filtration and ultrafiltration), methods depending upon diffusion, or upon Stokes' Law, estimations of the surface of particles and other special methods. It incidentally brings together a large number of interesting observations. There are 165 figures, mainly of apparatus, and the monograph is provided with indexes of authors, of subjects and of substances occupying altogether 55 pages. This is a volume which will provide indispensable information or save any amount of time for all those who happen to be concerned with any of the aspects of this general problem. It is interesting to note that this thorough yet concise treatment of this special subject is almost twice as lengthy as Svedberg's general monograph recently reviewed.

JAMES W. MCBAIN

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[CONTRIBUTION FROM THE JARVIS CHEMICAL LABORATORY, TRINITY COLLEGE]

THE TRANSITION TEMPERATURE OF CARBON TETRACHLORIDE AS A FIXED POINT IN THERMOMETRY

BY EVALD L. SKAU AND HARRY F. MEIER

RECEIVED FEBRUARY 4, 1929 PUBLISHED DECEMBER 11, 1929

In a recent paper[1] McCullough and Phipps have suggested the use of the transition point of carbon tetrachloride[2] as a fixed point in thermometry and have given this transition temperature as —48.54 ± 0.02'. For reasons which will appear below it seemed advisable to redetermine this transition temperature and the value found by us is —47.55 ± 0.12'.

Method,—Our observations were made by means of a special cooling curve and heating curve apparatus which will be described in detail in a paper now being prepared for publication by one of us (E. L. S.). The apparatus involves a cryostat whose temperature can be very accurately regulated and in which a 0.7–1.0 g. sample is suspended in an hermetically sealed "freezing point tube." The latter is made of extremely thin-walled glass tubing (0.05 mm. wall thickness) in order that its heat capacity may be negligibly small with respect to that of the sample, and is so constructed that the temperature of the sample may be followed by means of a single-junction thermocouple one element of which fits snugly into a thin-walled capillary tube extending down into the center of the sample. The cold junction is kept at 0°. The readings are made to the nearest microvolt (0.03') by means of a Leeds and Northrup Type K potentiometer.

Calibration and Materials.—The thermocouple, which is made of No. 30 constantan and No. 36 copper wire (B. and S. gage) was calibrated at the ice point, at the freezing point of pure mercury (−38.87°),[3] at the sublimation point of carbon dioxide (−78.51°)[3] and at the boiling point of oxygen (−183.00°).[3] The last two points were established by measuring the vapor pressure of the carefully purified substances in a

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[1] McCullough and Phipps, THIS JOURNAL, 50, 2213 (1928).

[2] The existence of this transition point was recognized previously by Goldschmidt [*Z. Krist.*, 51, 21 (1912); THIS JOURNAL, 50, 3390 (1928)] and by Latimer [*ibid.*, 44, 90 (1922)]. Neither of these investigators, however, was interested in the exact measurement of the transition temperature.

[3] "International Critical Tables," Vol. I, p. 53.

constant temperature cryostat in which the thermoelement was immersed.[4] In each case the purity of the sample was tested by evaporating to one-half volume and then redetermining the vapor pressure. The calibration at the mercury point was carried out in the same apparatus as the freezing points and under identical conditions.

In order to further corroborate the accuracy of our calibration in the range to be considered, we are recording below the freezing point data obtained by our method on samples of carbon tetrachloride and chlorobenzene kindly supplied to us "for thermocouple calibration" by Professor Jean Timmermans. This same sample of carbon tetrachloride was used for our determination of the transition point in question.

Results.—A number of cooling curves and heating curves were obtained on chlorobenzene at its freezing point, and on carbon tetrachloride at its freezing point and at its transition point. The data given in Cols. 2 and **3** of Table I are the values obtained from these curves using our own thermocouple calibration; those in Col. 4 are the values as determined independently by Timmermans on the same samples for the purpose of thermometric standardization.

TABLE I

FREEZING POINT AND TRANSITION POINT DATA

Substance	Phenomenon	Temperatures, °C. Heating curve	Cooling curve	Timmermans
Carbon tetrachloride	F. p.	−22.84	−22.87	−22.9
Chlorobenzene	F. p.	−45.20	−45.23	−45.2
Carbon tetrachloride	Tr. p.	−47.43	−47.67	......

It will be noted that whereas the freezing point values as obtained by the heating and cooling curves show very good agreement, the corresponding values for the transition point differ by 0.24°. It was found that the heating curve value was fairly reproducible but that the value obtained by cooling curves varied from −47.67 to −47.99°, depending on the conditions, that is, on the degree of supercooling and on the rate of cooling. In cases such as this, where one cannot establish equilibrium by stirring due to the fact that the change takes place in the solid state, it is, of course, to be expected that the proper degree of supercooling before the transition takes place is very important.[5] Our best curves for this point were obtained with a supercooling of 3 to 4°, the rate of cooling being about 0.3° per minute.

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[4] The details of this method have been fully described by Keyes, Townshend and Young, *J. Math. Phys. Mass. Inst. Tech.*, *1*, 3[illegible]2 (1922); see also Loomis and Walters, THIS JOURNAL, 48,3101 (1926), and Henning, *Ann. Physik,* 43,282 (1914).

[5] Nernst [Z. *physik. Chem.*, *15*, *681* (1894)] discusses the dangers of supercooling too little or too much in cryoscopic determinations in dilute solutions; see also Findlay's "Practical Physical Chemistry," 4th ed., Longmans, Green and Co., London, 1926, pp. 114–115.

Discussion

Our results show that the transition point of carbon tetrachloride is $-47.55 \pm 0.12°$; that is, it must lie between the temperature, $-47.43°$, the value obtained from heating curves, and $-47.67°$, the highest value from cooling curves.

The large discrepancy between our value for this point and that reported by McCullough and Phipps is probably not due to a difference in the purity of the sample used, judging from their freezing point data. It may be caused in part by the fact that their thermometer calibration at the sublimation point of carbon dioxide was not done by the accepted method. It is very likely chiefly due, however, to the inadequacy of their method of obtaining cooling curves, This seems probable at least from the fact that their diagram of the cooling curve for their best sample shows that there was no supercooling.

From the results of our investigation it seems improbable that the transition point of carbon tetrachloride will be entirely satisfactory for general use as a fixed point in thermometry. Except in the case of hydrates, transition points do not lend themselves to this purpose due to the difficulty of attaining a definite equilibrium in the solid state.[6]

We are indebted to the American Academy of Arts and Sciences for a grant from the Cyrus M. Warren Fund to carry out this work.

Summary

The transition point of carbon tetrachloride has been redetermined on a very pure sample in a special apparatus using a thermocouple whose calibration has been very carefully checked. The transition takes place at $-47.55 \pm 0.12°$, about one degree higher than reported by McCullough and Phipps.[1] This transition phenomenon is apparently not suitable as a fixed point for thermometry.

HARTFORD, CONNECTICUT

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[6] Wyatt [*Trans. Faraday Soc.*, *24*, 429 (1928); 25, 43, 48 (1929)] suggests the suspension of the carbon tetrachloride in a liquid for reproduction of a definite temperature at the transition point. On the basis of values so obtained he places the transition point of carbon tetrachloride at "about −48°C." He used a thermometer in his temperature measurements whose stem-emersion calibration was based upon McCullough and Phipps' value for the transition temperature. Timmermans [*Bull. soc. chim. Belg.*, 37,409 (1928)] has also worked on such binary systems and reports that the transition point of carbon tetrachloride in cyclohexane, chloroform and acetone is −46"; in carbon disulfide, −46.5'.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

STUDIES ON COMPLEX COMPOUNDS. I. REMOVAL OF AMMONIA FROM THE COORDINATION SPHERE[1]

BY H. I. SCHLESINGER AND RUBY K. WORNER

RECEIVED APRIL 29, 1929 PUBLISHED DECEMBER 11, 1929

Werner's theory accounts for and predicts clearly the changes which occur when three molecules of ammonia are successively removed from one molecule of a stable hexammine of a trivalent metal; what would happen if more ammonia were removed cannot be definitely foretold. Numerous possibilities present themselves—for example, the coordination number may change or various types of polynuclear compounds may be formed. We are reporting in this paper two such reactions; in one of them a polynuclear compound seems to be the product and in the other a hexacido compound is obtained. In later papers illustrations of change in coordination number will be described.

Cobaltic ammines do not lend themselves to investigations of this sort because they undergo complete decomposition when attempts are made to remove ammonia directly. Hexammine chromic salts are known to be readily convertible into pentammines, but what happens on further removal of ammonia has not been thoroughly studied. For this reason chloro pentammine chromic chloride was chosen by us as the starting material. When this substance is heated in air, in hydrogen, in carbon dioxide, or in ammonia, it decomposes into trichloro triammine chromium. This product, however, immediately reacts further to give a black compound unless the temperature is very carefully controlled.[2] If the pentammine is heated in a stream of dry hydrogen chloride, a very rapid reaction occurs at about 270° with considerable evolution of heat and is accompanied by a marked color change of the material from pink to green. If heating is discontinued at this point, the product washed with cold water to which a little hydrochloric acid has been added and then dried with alcohol and ether, a very insoluble green substance, *trichloro triammine chromium* is obtained.[3,4]

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[1] The material for this article is taken from a thesis presented in 1925 to the Faculty of the Ogden Graduate School of Sciences of the University of Chicago by Ruby K. Worner in part fulfilment of the requirements for the degree of Doctor of Philosophy. Since the completion of this research considerable further work has been done along these lines, and the report is therefore made very brief. For details not reported herein and aspects of the investigation omitted, reference is made to the thesis.

[2] Ufer, *Ann.* Chem., 112, 281 (1859), and Schrotter, Ann., 37, 148 (1841), report the formation of the black substance, which they describe as a nitride of chromium, and mention the intermediate formation of a green compound, the nature of which they failed to recognize.

[3] It is interesting to note that under no conditions does the pentammine lose but one molecule of ammonia to form tetrammine. Furthermore, the triammine, when

This triammine is markedly different from a substance of the same composition described by Werner.[5] His compound is blue green, dissolves fairly readily in warm water and especially easily in warm dilute hydrochloric acid to give a deep blue solution of trichloro aquo triammine chloride; ours is insoluble in hydrochloric acid or in water, but with the latter it slowly reacts to give a pink solution which has since been shown to contain diaquo tetrammine chromic chloride. Here evidently is a case of isomerism of a type not frequently encountered, but whether it is stereoisomerism, possible according to Werner's theory, or is what is often called "polymerization isomerism" cannot be decided because of the insolubility of the compounds in question.[6]

Attempts to remove some of the three remaining molecules of ammonia from the coordination sphere show the firmness with which chromium retains the coordination number 6. When the triammine is heated to 175° in a stream of hydrogen chloride, ammonia is not withdrawn from the compound, but hydrogen chloride is quantitatively absorbed to give a reddish-purple, very hygroscopic crystalline material which may be considered to be *ammonium chromic hexachloride.*[7] The substance is insoluble in all solvents except water, with which it reacts almost instantly to produce a deep green solution presumably of hydrated chromic chloride.[8]

Those who make a distinction between double and complex salts may prefer to class the substance just described with the former rather than to call it a salt of the complex $[CrCl_6]^{---}$ ion.[9] There are, however, several objections to this point of view. Anhydrous chromic chloride, alone or when mixed with ammonium chloride, reacts with liquid ammonia to give a mixture of hexammine and chloro pentammine chromic chlorides without the intermediate formation of a solution. What we have called ammonium chromic hexachloride dissolves readily in liquid ammonia to give

treated with liquid ammonia, gives pentammine directly, a reaction which requires weeks for completion. These reactions will be discussed further in later papers.

[4] *Anal.* Found for chromium, 24.81; Cl, 50.39; NH_3, 24.29. Calcd. for $[Cl_3(NH_3)_3Cr]$: Cr, 24.83, Cl, 50.79; NH_3, 24.39. All analyses reported in this paper represent averages of the results with from 3 to 5 samples.

[5] Werner, *Ber.*, 43,2286 (1910).

[6] The formation of tetrammines from the triammine here described when they are treated with water or even with acids is a very unusual type of reaction which will be described in more detail in a later paper. It suggests the possibility that these triammines are polynuclear. We are at present attempting to obtain a more soluble example of the type, but have not so far succeeded.

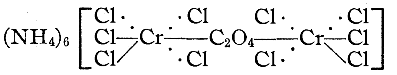
[7] *Anal.* Found: Cr, 16.33; Cl, 66.55; NH_3, 15.90. Calcd. for $(NH_4)_3[CrCl_6]$: Cr, 16.31; Cl, 66.73; NH_3, 16.00.

[8] Two stages in the reaction with water may be observed. At first a reddish solution is formed but this changes to green in a fraction of a second.

[9] No success attended attempts to prepare less soluble salts of this ion by double decompositions.

a green solution which is transformed to the pentammine only after complete evaporation of the liquid. Anhydrous chromic chloride reacts exceedingly slowly with dry gaseous ammonia; the new compound reacts rapidly at ordinary temperatures to give the pentammine. Double salts should possess a color which is the summation of the colors of the constituent salts; the compound here prepared is decidedly different in color from any known form of chromic chloride, the only colored constituent.[10]

In this instance, then, chromium, rather than changing its coordination number as the result of removal of ammonia, takes up hydrogen chloride, and the ammonia, although removed from the coordination sphere, remains in the molecule. A slightly different course is taken by the reaction when the compound *chloro oxalato triammine chromium* is treated as was the simple triammine. The oxalato compound is prepared quite simply by warming our trichloro triammine chromium with solutions of oxalic acid or of oxalates. It is a brick red, microcrystalline powder very insoluble in water or in acids, but when warmed with concentrated hydrochloric acid is reconverted into the triammine from which it was prepared.[11] At 190° it reacts slowly with gaseous hydrogen chloride. When the material attains constant weight, its composition always corresponds to the empirical formula $2CrCl_3 \cdot (NH_4)_2C_2O_4 \cdot 4NH_4Cl$.[12] According to Werner's theory this might be formulated as



in other words, a compound of polynuclear type. Its properties are similar to those of ammonium chromic chloride except that it reacts somewhat

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[10] If trichloro triammine chromium is heated at 270°, instead of 175°, in a stream of hydrogen chloride, a rapid reaction occurs and continues until the composition of the material corresponds to the formula $2CrCl_3 \cdot 3NH_4Cl$. (*Anal.* Found: Cr, 21.76; Cl, 66.54; NH_3, 10.85. Calcd.: Cr, 21.79; Cl, 66.87; NH_3, 10.70.) Thereafter reaction is very slow and leads to anhydrous chromic chloride. On account of the difference in the rate of reaction before and after the attainment of the composition mentioned, the material can be isolated in fairly pure condition. It is purple in color, but also reacts with water to give hydrated chromic chloride. The fact that this substance has a markedly different color from that of the ammonium chromic chloride shows that we are not dealing with double salts of an unknown form of chromic chloride, for, if that were the case, both double salts should possess the same color. It might be mentioned that in the preparation of trichloro triammine chromium by the method described, some of the purple compound is always obtained. It is removed completely by washing the mixture with cold water.

[11] Further details of this reaction, which leads to rather unusual results when slightly varied, will be described in a later paper. Analytical data are as follows: calcd. for $ClC_2O_4(NH_3)_3Cr$: Cr, 22.96; Cl, 15.65; NH_3, 22.54; C_2O_4, 38.83. Found: Cr, 22.89; Cl, 16.02; NH_3, 22.24; C_2O_4, 38.74.

[12] *Anal.* Calcd.: Cr, 15.89; Cl, 54.16; NH_3, 15.60; C_2O_4, 13.44. Found: Cr, 16.37; Cl, 54.40; NH_3, 15.45; C_2O_4, 13.38.

more slowly with water, although the reaction is still too rapid to permit studies of constitution.[13]

Summary

1. The new substances $[Cl_3(NH_3)_3Cr]$, $[ClC_2O_4(NH_3)_3Cr]$, $(NH_4)_3[CrCl_6]$, and $(NH_4)_6[Cr_2C_2O_4Cl_{10}]$ are prepared and described. The first is an isomer of the trichloro triammine chromium prepared by Worner.

2. The removal of ammonia from the coordination sphere of chromium is briefly discussed.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

STUDIES ON COMPLEX IONS. II. THE PREFERENTIAL REMOVAL OF BROMIDE ION FROM THE COORDINATION SPHERE[1]

BY H. I. SCHLESINGER AND D. N. RICKLES

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In order to study the relative tendency of various simple negative ions to become a part of complex positive ions, attempts have been made in this Laboratory to prepare compounds of the type $[CrR_3X_1X_2X_3]$ in which R represents a non-ionic constituent and X_1, X_2 and X_3 are univalent negative ion constituents. The determination of which one of the ionic constituents is driven out in preference to the others by the addition of one or two moles of R per mole of the compound would give evidence of the relative ability of each simple negative ion to form complex positive ions with chromium. A number of compounds having empirical formulas of the character mentioned have been prepared, but some additional data recently obtained have raised the question whether these substances, all of which are insoluble in all solvents, are not perhaps compounds of more complex type. For these reasons, the experimental results only are described in this paper and their interpretation is deferred to a later time.

Following the procedure of Schlesinger and Worner[2] the three "triammines" $[Br_3(NH_3)_3Cr]_x$, $[ClBr_2(NH_3)_3Cr]_x$, and $[Cl_2Br(NH_3)_3Cr]_x$ were prepared by thermal decomposition of the appropriate pentammine at 175°. The green products thus obtained were thoroughly washed with

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[13] The formation of this compound again suggests that the triammines here described may really have a more complex structure than the name employed implies.

[1] This article is a résumé of a thesis presented by D. N. Rickles to the Graduate Faculty of the University of Chicago in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Schlesinger and Worner, THIS JOURNAL, 51,3520 (1929).

water until the washings were colorless. The residues were then dried with alcohol and ether. The properties of the compounds are similar to those of trichloro triammine chromium described by Schlesinger and Worner.[2]

Anal. Calcd. for $[Br_3(NH_3)_3Cr]_x$: Cr, **15.17;** NH_3, **14.91;** Br, **69.93.** Found: Cr, **14.83;** NH_3, **15.54;** Br, **70.86.** Calcd. for $[ClBr_2(NH_3)_3Cr]_x$: Cr, **17.43;** NH_3, **17.12;** Cl, **11.88;** Br, **53.57.** Found: Cr, **17.43;** NH_3, **17.64;** Cl, **12.00;** Br, **53.74.** Calcd. for $[Cl_2Br(NH_3)_3Cr]_x$: Cr, **20.48;** NH_3, **20.12;** Cl, **27.93;** Br, **31.47.** Found: Cr, **19.72;** NH_3, 19.36; Cl, 27.81; Br, **31.43.**

Compounds of this series containing iodo, nitrato or nitrito groups could not be prepared in this manner nor by removing water from aquo triammines.[3]

Dihalido Tetrammine Chromic Salts, ***(Cis*** (?)-Type).—Ten cc. of hydrobromic acid (sp. gr. 1.20) was added to 1 g. of chloro oxalato triammine chromium,[2] $[Cl\cdot C_2O_4\cdot(NH_3)_3Cr]$, and the mixture was boiled until the lavender oxalato triammine was completely converted to a dark green material. The green compound was collected on a filter, while the reaction mixture was still warm, washed with dilute hydrobromic acid and dried with alcohol and ether. The compound was purified by reprecipitating it with hydrobromic acid (sp. gr. 1.70) from its saturated aqueous solution; yield, 0.72 g. That the bromine is not coordinated with chromium is shown by the method of recrystallization and by the fact that the bromine can readily be replaced by double decomposition.

Anal. Calcd.: Cr, **19.19;** NH_3, **25.15;** Cl, **26.17;** Br. **29.94.** Found: Cr, **19.01;** NH_3, 24.85; Cl, 25.66; Br, **28.80.**

When carefully heated the tetrammine decomposes into "dichloro bromo triammine chromium" and a purple substance not further investigated; it reacts with ammonium oxalate to give "chloro oxalato triammine chromium"—a reverse of the reaction by which it is prepared—and by double decomposition to give dichloro tetrammine *chloride, iodide* and other similar salts. The iodide may also be prepared by treating "chloro oxalato triammine" chromium with boiling hydriodic acid (sp. gr. 1.50) free from iodine.[4] Further reactions need not be described as they have no bearing on this paper.

The corresponding dibromo tetrammine chromic bromide, $[Br_2(NH_3)_4Cr]Br$, the preparation of which is important for reasons which will be-

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[3] In this connection it was noted that when dichloro aquo triammine chromic nitrate was heated in ordinary air at 100°, it took on water, instead of losing it. This extraordinary stability of aquo compounds is unexpected.

[4] If the hydriodic acid contains free iodine, the reaction yields, instead of the green tetrammine, a well crystallized brown substance from which iodine is freely evolved when heat is applied. It dissolves in water to give a brown solution which slowly turns green and contains free iodine. Organic solvents such as chloroform and ether extract no iodine from it. It also is a tetrammine but has not yet been further characterized.

come obvious later, was obtained by treatment of bromo oxalato triammine chromium with hydrobromic add, Details of purification and the properties correspond exactly to those for the analogous chlorine derivatives except in one respect.[5] Unlike the chlorotetrammines, the green bromo tetrammines give a red solution in water, but this change is not a transformation into the isomer to be described below. From the red solution the green tetrammine may be reprecipitated either by the addition of alcohol-ether **mixtures** or of hydrobromic acid, provided the solution is freshly prepared. After the solution has stood for several days both of these reagents precipitate from it red diaquo tetrammine chromic bromide. Obviously the hydration begins as soon as the solution is prepared, but is a slow reaction. Further evidence that the green bromo tetrammine is of the same type as the chloro tetramrnine is found in the fact that both react with oxalic acid to give halido oxalato chromium compounds.

Trans (?) Dibromo Tetrammine Chromic Bromide.—When "tribromo triammine chromium" is heated with hydrobromic acid (sp. gr. 1.20), a reddish-brown mixture of a tetrammine and a pentammine is obtained.[6] The two components may be separated by treating the mixture with a small amount of ice water, and filtering the solution rapidly. The pink pentammine remains undissolved, and the tetrammine may be reprecipitated by the addition of hydrobromic acid (sp. gr. 1.70) to the solution. Re-solution and reprecipitation effect purification. Analysis leads to the formula $[Br_2(NH_3)_4Cr]Br$.

And. Calcd.: Cr, 14.45; NH_3, 18.93; Br, 66.62. Found: Cr, 14.46; NH_3, 19.21; Br, 67.22.

This tetrammine, in contrast to the others described, is dark red instead of green. It dissolves in water to give a red solution, as does the green dibromo tetrammine chromic bromide, but from the solution of the red tetrammine the original substance, not an aquo compound, is precipitated by addition of hydrobromic acid or by alcohol-ether mixtures. The red tetrammine is neither formed from nor does it give "bromo oxalato triammine chromium." It may be noted that the transformation of one type of the tetrammine into the other, a very common reaction in other cis and *trans* series, does not seem to occur with the compounds here described under any conditions we have observed. We have provisionally assigned the cis structure to the green tetrammines because they are formed from and can readily be converted to oxalato compounds. Inasmuch

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[5] Bromo oxalato triarnmine was prepared by heating tribromo triammine chromium with ammonium oxalate. Analyses of the various compounds mentioned in this paragraph as well as other details are described in the thesis of Dr. Rickles (University of Chicago, 1928).

[6] The pentammine is formed directly from the triammine, for the pure tetrammine does not yield pentammine under analogous conditions. Obviously the reaction of triammines with acids is very complex,

as the reaction involves a transformation of a triammine to a tetrammine or vice versa, in other words a very deep-seated change in the complex ion, the basis for this conclusion is not as secure as might be desired. In fact, there is some evidence which might be considered to favor the opposite interpretation. Oxalato tetrammine chromium[7] compounds are orange-red. Oxalato compounds are always assumed to be the cis type; hence, the red bromo tetrammine might also be considered to be of this structure; but we have preferred to lay more weight on the evidence obtained from its reactions than on that based on color similarities, because it is well known that substitution of different groups in complex ions is very often responsible for color changes.

Possible Structure of the "Triammines."—The reactions of the "triammines" with acids to give tetrammines, as described above, suggests the possibility that they are polymerization complexes which contain a tetrammine ion. Thus what we have called trichloro triammine chromium $[Cl_3(NH_3)_3Cr]$, may be a compound such as $[Cl_2(NH_3)_4Cr]$ $[Cr(NH_3)_2Cl_4]$. There are, on the other hand, rather serious objections to formulas of this type. In the first place, it would be difficult to explain on this basis why in a single reaction the compound, $[Br_3(NH_3)_3Cr]$, should yield both a triammine and a pentammine. In the second place, the formulation suggested would not explain why the tetrammines yield triammines on heating, for a reaction such as

$$2[Cl_2(NH_3)_4Cr]Cl \longrightarrow [Cl_2(NH_3)_4Cr][Cr(NH_3)_2Cl_4] + 2NH_3$$

seems highly improbable. The question is being further investigated.[8]

Reaction of Oxalates with Mixed Halide Complexes.—One gram of $[Cl_2Br(NH_3)_3Cr]_x$ was heated with 5 cc. of a saturated aqueous solution of ammonium oxalate and a solid was obtained which was apparently $[ClC_2O_4(NH_3)_3Cr]_x$.

Anal. Calcd. for $[ClC_2O_4(NH_3)_3Cr]$: Cr, 22.92; NH_3, 22.45; Br, 0.00; Cl, 15.64. Composition of solid: Cr, 22.04; NH_3, 21.90; Br, 0.06; Cl, 16.09.

The low results for chromium and ammonia, the high value for chlorine and the presence of a slight trace of bromine in the reaction product, all point to a slight amount of unchanged starting product rather than to admixture with $[BrC_2O_4(NH_3)_3Cr]_x$. This result suggests that bromo groups are more readily removed from the coördination sphere than chloro groups, but until the exact character of the hypothetical triammines has been established, this conclusion cannot be considered as definitely proved.

The treatment of the compound $[ClBr_2(NH_3)_3Cr]_x$ with ammonium oxalate in the same manner leads to the formation of mixtures.

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[7] P. Peiffer, Ber., 38, 3598 (1905).

[8] Recently we have discovered a new type of "triammine" which is pink instead of green and which yields hexammines on treatment with acids.

Anal. Calcd. for $[ClC_2O_4(NH_3)_3Cr]$: Cr, 22.92; NH_3, 22.45; Cl, 15.64; Br, 0.00. Calcd. for $[BrC_2O_4(NH_3)_3]Cr$: Cr, 19.17; NH_3, 18.80; Cl, 0.00; Br, 29.42. Analysis of reaction product: Cr, 21.10; NH_3, 21.20; Cl, 10.96; Br, 10.42.

The indications are that a larger percentage of the chloro compound was obtained, but exact calculations are impossible because of the presence of unknown amounts of the starting product. In general the results corroborate the tentative conclusion reached above.

Reaction of Mixed Triammines with Ammonia.—Dry ammonia at atmospheric pressure and 200° passed over the triammines $[ClBr_2(NH_3)_3Cr]$, and $[Cl_2Br(NH_3)_3Cr]_x$ produces mixtures of pentammines. The analytical results need not be given here since they do not permit calculation of the relative amounts of the various pentammines, but when air was mixed with the ammonia in such proportion as to reduce the partial pressure of ammonia to 182 millimeters (as determined by measuring the proportion of the two components by two flowmeters) only $[Br_2Cl(NH_3)_3Cr]_x$ reacted to give appreciable quantities of pentammine in from fifty to seventy hours. The reaction product was washed with water and the aqueous filtrate was treated with ammonium oxalate to precipitate the oxalate of the pentammine. In this way ionized halogen is removed from the compound, thus making the identification of the halogen group in the coordination sphere more exact. Only chloride was present; the quantitative analysis yielded 13.73% of chlorine, in good agreement with 13.62% required for the chloro pentammine chromic oxalate. Again these results suggest that the bromo group is more readily displaced from the complex, but in this case this conclusion is warranted only if the starting products are simple triammines. The interpretation of the results will be given in a later paper.

Summary

1. Several new "triacido triammine chromic" salts, $[Br_3(NH_3)_3Cr]_x$, $[Br_2Cl(NH_3)_3Cr]_x$, $[BrCl_2(NH_3)_3Cr]_x$ and $[Br\cdot C_2O_4\cdot(NH_3)_3Cr]_x$ have been prepared.

2. A method of obtaining chloro and bromo tetrammine chromic salts, hitherto unknown, has been devised. Both cis and *trans* salts have been obtained.

3. The action of mixed "triammines" such as $[ClBr_2(NH_3)_3Cr]$ with ammonia and with oxalates has been studied. In all cases the bearing of the results on the question of the factors which determine the stability of complex ions will be taken up in later papers.

CHICAGO, ILLINOIS

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

AN ISOTOPE OF OXYGEN, MASS 17, IN THE EARTH'S ATMOSPHERE

BY W. F. GIAUQUE AND H. L. JOHNSTON

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Recently[1,2] the presence of an oxygen isotope, mass 18, in the earth's atmosphere, was reported. In this paper it will be shown that an additional isotope of oxygen with mass 17 is also present. As in the previous case, the conclusion is based on a study of atmospheric absorption spectra obtained by H. D. Babcock of Mount Wilson Observatory. Since our interpretation of the weak A' band in the atmospheric absorption of sunlight as originating from the 18–16 oxygen molecule, Babcock has carried out further measurements which have supplied additional support by extending the various branches of the bands. He has also found a new series of very weak lines. Babcock has kindly permitted us to make use of his manuscript in advance of publication.[3] He suggests that this new series is due to the forbidden alternate rotation levels of the 16–16 oxygen molecule, although, as he states, they do not occupy the correct positions by many times the experimental error.

We have found that these lines originate from an oxygen molecule consisting of an atom of mass 17 in combination with one of mass 16. In agreement with the predictions of the theory of wave mechanics the normal state of this molecule has one-half unit of vibration and both odd and even rotation levels exist.

The method of calculation of the isotopic separation of the lines makes use of the equations given for this purpose by Loomis.[4] In calculating the vibrational isotope effect we have previously made use of the equation given by Birge[6] for the normal oxygen molecule, namely

$$\nu^n = 1565.37\% - 11.37n^2$$

and that given by Dieke and Babcock[6] for the 1.6 volt level as

$$\nu^n = 1415.017\, n - 11.91\, n^2 - 0.3525\, n^3$$

Birge[7] has recently found that the latter equation is incorrect due to an error in computation and should be

$$\nu^n = 1418.69\, n - 13.925\, n^2 - 0\ 02\, n^3$$

where $n = 0, 1, 2, \ldots.$

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[1] Giauque and Johnston, *Nature*, 123,318 (1929).

[2] Giauque and Johnston, THIS JOURNAL, 51,1436 (1929).

[3] Babcock, *Proc. Nat. Acad. Sci.*, 15, 471 (1929).

[4] Loomis, *Bull. Natl. Research Council*, 11, Chap. V (1926).

[5] Birge, *ibid.*, 11, Chap. V (1926).

[6] Dieke and Babcock, *Proc. Nat. Acad. Sci.*, 13,670 (1927).

[7] Birge, *Nature*, in press.

As a result of this observation Birge shows that the systematic difference of observed and calculated isotopic effects which occurred in our calculations on the 18–16 molecule is practically eliminated, and demonstrates the remarkable accuracy of the measurements of Dieke and Babcock.[6]

On the basis of the two vibration equations given by Birge, the data for the 18–16 molecule have been recalculated.

The above vibrational formulas should be transposed so that the state given as zero corresponds to $n = {}^1/_2$ as required by the theory of wave mechanics.

The formulas for the separation of the P and R branches of the 18–16 and 16–16 molecules are as follows

$$\Delta\nu_P = 2.07 + 0.0556\,[B''m^2 - \beta''m^4 - B(m-1)^2 + \beta'(m-1)^4]$$
$$\Delta\nu_R = 2.07 + 0.0556\,[B''m^2 - \beta''m^4 - B'(m+1)^2 + \beta'(m+1)^4]$$
$$m = 1/2, 3/2, 5/2, \ldots$$

For the separations of the lines due to the 17–16 and 16–16 molecules

$$\Delta\nu_P = 1.09 + 0.0294\,[B''m^6 - \beta''m^4 - B'(m-1)^2 + \beta'(m-1)^4]$$
$$\Delta\nu_R = 1.09 + 0.0294\,[B''m^2 - \beta''m^4 - B(m+1)^2 + \beta'(m+1)^4]$$

The constants as given by Dieke and Babcock[6] are

$$B'' = 1.438 \qquad \beta'' = 6.31 \times 10^{-6}$$
$$B' = 1.390 \qquad \beta' = 5.75 \times 10^{-2}$$

The lines calculated for the 16–18 and 16–17 molecules are given beside the observed data in Table I. In order to clear up any doubt concerning

TABLE I

CALCULATED AND OBSERVED LINES IN THE A BANDS OF THE 16–18 AND 16–17 OXYGEN MOLECULES

P$_1$ Branch

	Cm.$^{-1}$ 16-16		Cm.$^{-1}$ 16-18		Cm.$^{-1}$ 16-17	
j'	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
0	13,118.06	13,118.04	13,120.29	13,120.29	13,119.24	
1	*115.04*	*115.45*	117.44	117.50	116.31	13,116.28
2	111.99	112.02	114.56	114.59	113.35	
3	*108.85*	*109.14*	111.59		110.30	110.38
4	105.58	105.64	108.50	108.55	107.13	
5	*102.28*	*102.54*	105.39		103.93	103.97
6	098.83	098.87	102.13	102.16	100.58	
7	*095.35*	*095.61*	098.84		097.20	097.36b
8	091.73	091.72	095.43	095.42	093.70	
9	*088.03*	*088.32*d	091.94		090.11	090.07
10	084.23	084.22	088.35	088.32b,d	086.43	
11	*080.33*	*080.67*	084.67	084.60b	082.63	082.60
12	076.34	076.34	080.90	080.89	078.77	078.92b
13	*072.28*	*072.70*	077.06	077.02	074.83	074.78
14	068.13	068.10	073.14	073.11	070.81	070.94b
15	*063.84*	*064.22*	069.09	069.02	066.64	066.80b,d
16	059.45	059.47	064.96	064.97	062.40	
17	*055.02*		060.78	060.71	058.10	

TABLE I (*Continued*)

	Cm.$^{-1}$ 16–16		Cm.$^{-1}$ 16–18		Cm.$^{-1}$ 16–17	
j′	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
18	050.49	050.48	056.50	056.48	053.70	
19	***045.86***		052.12		049.21	
20	041.12	041.13	047.65	047.67		
21	***036.32***		043.12			
22	031.40	031.40	038.47	038.46		
23	***026.39***		033.74	033.65		
24	021.29	021.29	028.93	028.88		

P$_2$ Branch

j′	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
0	***13,120.15***	Excluded	***13,122.38***	Excluded	***13,121.33***	Excluded
1	***117.13***	***13,116.28***	119.53	13,119.64	118.40	
2	114.07	114.11	116.64	116.62	115.43	13,115.45
3	***110.93***	***110.38***	113.67	113.56	112.38	
4	107.68	107.63	110.60	110.56	109.23	109.14
5	***104.32***	***103.97***	107.43		105.97	
6	100.89	100.81	104.19	104.13	102.64	102.54
7	***097.36***	***096.82***	100.85		099.21	
8	093.72	093.64	097.42	097.36b	095.69	095.61
9	***090.00***	***090.07***	093.91		092.08	
10	086.18	086.12	090.30	090.25	088.38	088.32b,d
11	***082.27***	***082.60***	086.61	086.57	084.57	084.60b
12	078.26	078.22	082.82	082.79	080.69	080.67
13	***074.18***	***074.78***	078.96	078.92b	076.73	
14	069.99	069.96	075.00	074.97	072.67	072.70
15	***065.71***	***066.80***	070.96	070.94b	068.51	
16	061.32	061.34	066.83	066.80b,d	064.27	064.22
17	***056.85***	***056.48***	062.61	062.60	059.93	
18	052.30	052.34	058.31	058 35	055.51	
19	***047.64***	***047.67***	053.91	053.94	050.99	
20	042.92	042.95	049.45	049.45	046.37	
21	***038.09***		044.89	044.91		
22	033.20	033.21	040.27	040.20		
23	***028.16***		035.51	035.55		
24	023.09	023.09	030.73	030.74		

R$_1$ Branch

j′	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
1	***13,123.77***	***13,123.95***	13,125.69		13,124.78	13,124.78
2	126.37	126.40	128.14		127.30	127.42
3	***128.99***	***129.14***	130.59	13,130.49	12983	
4	131.48	131.51	132.96		132.25	
5	***133.90***	***134.18***	135.25	135.26	134.60	
6	136.24	136.21	137.46	137.49	136.87	
7	***138.47***		139.56	139.49b,d	139.03	
8	140.59	140.60	141.57	141.55b	141.09	
9	***142.63***		143.49	143.54b,d	143.07	143.0
10	144.57	144.54	145.33	145.29	144 95	
11	***146.44***		147.09	147.01b	146.76	
12	148.17	148.13	148.73	148.72b,d	148.45	148.60d
13	***149.51***		150.28		150.04	

TABLE I (*Concluded*)

	Cm.$^{-1}$		Cm $^{-1}$		Cm.$^{-1}$	
	16–16		16–18		**16-17**	
j'	**Calcd.**	**Obs.**	**Calcd.**	**Obs.**	**Calcd.**	**Obs.**
14	151.38	151.35	151.77		151.57	
15	*152.83*		153.14		152.97	
16	154.17	154.12	154.41		154 27	
17	*155.44*		155.61	155.64b	155.53	155.64b
18	15663	156.43	156.76			
19	*157.72*		157.79	157.75b		
20	158.72	15872	15874			
2i	*159.61*		159.50	15953		
22	160.39	160.38	160.33			
23	*161.06*		160.97			
24	161.61	161 62	161.48			
25	*162.08*		161.92	161.93		
26	162.51	162.51	162 32			
27	*162.92*		162.71			
			R_2 Branch			
1	*13,125.68*	*13,124.78*	*13,127 60*	Excluded	*13,126.69*	Excluded
2	128.31	128.28	130.08	13,130.09	129.24	13,129.14
3	*130.94*	*130.49*	132.54	132.55	131.78	
4	133.43	133.45	134.91	134.94	134.20	134.18
5	*13587*	*135.26*	137.22	137.26	136.57	
6	138.20	138.22	139.42	139.49b,d	138.83	
7	*140.46*	*139 49*	141.55	141.55b	141.02	
8	142.60	142.61	143.58	143.54b,d	143.10	
9	*144.64*		145.50	145.50	145.08	
10	146.62	146.61	147.38	147.35	147.00	147.01b
11	*148.48*	*148.60*	149.13	149.10	148.80	148.72b,d
12	150.21	150.22	150.77	150.77	150.49	
13	*151.87*	*151.95*	152.34	152.34	152.10	151.95
14	153.43	153.50	153 82		153.62	
15	*154.91*		155.22	155.23b	155.05	155.23b
16	156.28	156.43	156 52		156.38	
17	*157.56*		157.73	157.75b,b	157.63	157.75b,b
18	158.75	158.72	158.87			
19	*159.86*		159.93	159.91		
20	160.86	160.85	160.88			
21	*161.74*		161.72	161.62		
22	162.52	162.51b	162.46			
23	*163.20*		163.11	162.99		
24	163.79	163.81	163.66			
25	*164.30*		164.14	164.18		
26	164.71	164.70	164.53			
27	*165.10*		164.89	164.95		

the possibility that the new very weak lines might be due to the forbidden alternate rotation levels of the 16–16 molecule, the positions of the forbidden lines are calculated and given in italics along with the assignments of Babcock, also in italics, in Table I.

$$j(P) = m - 1/2 \qquad j'(R) = m + 1/2$$

where j' refers to the rotation levels of the upper electronic state. In addition to the change made in the 16–18 calculated values introduced by the use of the corrected vibrational wave number referred to above, several of the values at the bottom of the R branches have been changed slightly to conform with smooth values of the 16–16 molecule.

Excluding all lines that have been used in more than one place, the algebraic sum of the residuals has been calculated and divided by the number of lines to show the smallness of any systematic deviation. For the 16–18 band we obtain from 54 lines the value -0.012 cm.$^{-1}$ with a maximum deviation of -0.11 cm.$^{-1}$. For the 16–17 band, which is fainter and therefore harder to measure, a consideration of 20 lines leads to -0.018 cm.$^{-1}$ with maximum deviations of -0.15 cm.$^{-1}$ and $+0.15$ cm.$^{-1}$.

As was shown by Mulliken,[8] to whom the interpretation of the 16–16 band is due, the line corresponding to $j' = 0$ of the P_2 branch is excluded. This line is also experimentally absent for the 16–16 and 16–17 molecules. Professor Mulliken has called our attention to a paper by Kramers[9] in which it is shown that for the oxygen molecule the wave mechanics leads to *a* single level for the state where j''_K (rotational quantum number) $= 0$, although the higher levels are triplet in character. As Mulliken points out, this excludes the line corresponding to $j' = 1$ for the R_2 branches of the 16–18 and 16–17 molecules. In the previous treatment[2] of the 16–18 band we placed the line 13,127.42 in one of these positions with the notation that the poor agreement was possibly due to a beginning state anomaly. However, it now appears probable that the above exclusion is correct. The corresponding line for the 16–17 molecule is absent. The line 13,127.42 is in fair agreement with the $j' = 2$ line of the R_1 branch for the 16–17 molecule but there is doubt as to whether this entirely explains its presence since the intensity is much greater than that of the other 16–17 lines. There is, of course, always the possibility that, like a number of other lines intermixed with the oxygen bands, it has some origin other than the oxygen molecule.

Babcock[3,10] has carried out some very accurate intensity measurements to make an estimation of the relative amount of Isotope 18. We are somewhat doubtful regarding the assumption that relative absorption can be used as an exact measure of amount, for, as previously pointed out,[2] the isotopic molecules may be slightly polar due to zero point vibration of the unsymmetrical masses. Such polarity may increase the absorption coefficients of the 18–16 and 17–16 molecules. The values obtained from intensity measurements should be maximum amounts.

It should be possible to obtain information on the question of the effect of unsymmetrical masses on the absorption coefficient in the following

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[8] Mulliken, Phys. Rev., 32, 880 (1928).

[9] Kramers, *Z. Physik*, 53, 422 (1929).

[10] Babcock, *Nature*, 123, 761 (1929).

manner. Since electrical dissymmetry results from the vibration of the molecule, a greater effect would be expected for greater amounts of vibration. If intensity measurements on bands resulting from a higher state of vibration were carried out, it is possible that the absence of the above effect might be demonstrated or, if it proved to be real, the data might permit a correction.

Babcock estimates that the 18–16 molecules are present to the extent of one part in 1250 and therefore that oxygen contains one part of Isotope 18 in 2500. However, as previously mentioned,[2] a factor of 2 enters into this calculation, due to the fact that the 18–16 molecules have twice as many states in which to exist as have the 16–16 molecules, thus leading to a corresponding reduction in line intensity. When this factor is considered Babcock's results lead to one part in 625 for the 18–16 molecules and the Oxygen 18 atoms are present to the extent of one part in 1250, as a maximum.

From Babcock's estimate of the relative intensity of the lines due to the 17–16 molecules, we estimate the abundance of Oxygen 17 as about one part in 10,000 as a maximum.

Oxygen of mass 17 has been reported by Kirsch and Pettersson,[11] by Blackett,[12] and by Harkins and Shadduck[13] from data obtained on collisions between alpha particles and nitrogen nuclei. One or two collisions per hundred thousand result in combination of the alpha particle with the nitrogen, forming an unstable isotope of fluorine which immediately ejects a proton and becomes Oxygen 17. Blackett assigned a life of less than 10^{-10} sec. to Fluorine 18. Blackett also showed from the time factor in his fog track experiments that Oxygen 17 had a life of at least one-thousandth of a second.

We wish to thank Professor R. T. Birge for his friendly interest in the work and for calling attention to the collision experiments leading to Oxygen 17.

Summary

A new weak band recently discovered in the atmospheric absorption of oxygen by Mr. H. D. Babcock of Mount Wilson Observatory has been explained and shows that an isotope of oxygen of mass 17, as well as the previously discovered Oxygen 18, is present in the earth's atmosphere. On the basis of accurate intensity measurements by Babcock, 18–16 molecules are present to the extent of one part in 625 and 17–16 molecules to the extent of about one part in 5000. Thus Oxygen 18 has an abun-

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[11] Kirsch and Pettersson, *Arkiv. Mat. Astron. Fysik,* **19,** 15, **1–16 (1925);** ***Physik. Z.,*** **26,457 (1925).**

[12] Blackett, ***Proc. Roy. Soc. (London),*** **107A, 349 (1925).**

[13] Harkins and Shadduck, ***Nature,*** **118, 876 (1926);** ***Proc. Nab. Acad. Sci.,*** **12, 707 (1926).**

dance of one part in 1250 and Oxygen 17 about one part in 10,000. All of the above figures are maximum estimates.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

FURTHER EXPERIMENTAL TESTS OF THE GIBBS ADSORPTION THEOREM. THE STRUCTURE OF THE SURFACE OF ORDINARY SOLUTIONS

BY JAMES W. MCBAIN AND ROBERT DUBOIS

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The present investigation was undertaken to determine by direct measurement the absolute amounts of various solutes adsorbed, or concentrated, at the air–solution interface. The experimental results throw further light on the structure of surface layers of solutions and in addition furnish data for the test of the validity of the Gibbs adsorption equations both in their strict form and in the approximate form commonly used. They fully substantiate the experimental findings of McBain and Davies[1] for the large amounts of solute transported on a moving bubble. It is now undeniable that a bubble moving through a solution actually transports far more solute than can be close packed into a monomolecular layer on its surface, and several fold greater than the amounts predicted from the classical theorem of Gibbs.

The Gibbs adsorption theorem may be expressed in the equivalent form

$$\Gamma = -\frac{\mathrm{d}\sigma}{RT\,\mathrm{d}\ln a} = -\frac{a}{RT} \times \frac{\mathrm{d}\sigma}{\mathrm{d}a}$$

or, approximately

$$\Gamma = -\frac{\mathrm{d}\sigma}{RT\,\mathrm{d}\ln c} = -\frac{c}{RT} \times \frac{\mathrm{d}\sigma}{\mathrm{d}c}$$

where a is the activity of the solute and c its concentration, R is the gas constant, and T is the absolute temperature (Γ, R and a or c being expressed, of course, in consistent units); $\mathrm{d}\sigma/\mathrm{d}c$ is the slope of the surface tension/-concentration curve at the concentration c.

These equations, particularly the last, have been used by numerous writers to calculate the surface concentrations of many substances. The results so obtained have generally been accepted with singular confidence in lieu of actual measurement and are still used as the basis of extensive deductions as to the structure of interfacial adsorption layers and of solution surfaces. It was and is of importance, therefore, that the validity of the equations should be tested experimentally. So far the evidence has been decidedly adverse. Agreement in one case cannot obscure disagreement in all others.

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[1] J. W. McBain and G. P. Davies, THIS JOURNAL, 49, 2230 (1927).

Previous Experimental Tests of the Gibbs Theorem.—Experimental determinations of adsorption at fluid–fluid interfaces have been made by a number of workers, and these are collected in Table I. However, as McBain and Davies have proved, none of the results obtained by earlier workers has recorded the actually much larger amounts of solute transported by moving bubbles. This is due to the fact that all the solution, even that resulting from the collapse and escape of the bubbles, was con-

TABLE I

A SUMMARY OF PREVIOUS WORK

Worker	Interface	Solutes studied	Comparison of obs. and calcd. "Gibbs' adsorption"
Milner[2]	Air–water	Sodium oleate	No comparison made
Lewis[3]	Oil–water	Non-electrolytes	Obs. 15 to 70 times calcd.
		Inorganic electrolytes	Obs. 6 to 30 times calcd.
	Hg–water	Aniline, caffeine, sodium glycocolate, Hg_2SO_4	Obs. 3 to 25 times calcd.
Donnan and Barker[4]	Air–water	Nonylic acid, Saponine	Agreement claimed[a]
Griffin,[5] van der Meulen and Rieman,[6] Harkins[7]	Oil–water	Soaps	No comparison made
Oliphant and Burdon[8]	Hg–H_2O or Hg–A	Carbon dioxide	No comparison made
Schofield[9]	Hg–H_2O	Mercurous salts	Agreement claimed[10]
McBain and Davies[1]	Air–water	*p*-Toluidine	Obs. 2 times calcd.[b]
		Amyl alcohol	Obs. 4 times calcd.[b]
		Camphor	Obs. 3 times calcd.[b]
Laing, McBain and Harrison[11]	Air–water	Sodium oleate	Obs. greater than calcd. and twice monomolecular adsorption
Harkins and Gans[12]	Air–water	Nonylic acid	Approximate agreement[a]
		Amyl alcohol	Obs. 3 times calcd.[b]

[a] Pumping action occurring in these experiments as well as others not marked.

[b] Pumping avoided.

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[2] S. R. Milner, *Phil. Mag.*, [6] **13,** 96 (1907).

[3] W. C. McC. Lewis, *ibid.*, [6] **15,** 499 (1908); **17,** 466 (1909); *Z. physik.* Chem., **73,** 129 (1910); *Science Progress*, **11,** 199 (1916).

[4] F. G. Donnan and J. T. Barker, *Proc.* Roy. *Soc. (London),* **85A,** 557 (1911).

[5] E. L. Griffin, THIS JOURNAL, **45,** 1648 (1923).

[6] P. A. van der Meulen and Wm. Rieman, *ibid.*, **46,** 876 (1924); **47,** 2507 (1925).

[7] W. D. Harkins, "Colloid Symposium Monograph," Vol. V, **1927,** p. 19.

[8] M. L. Oliphant and R. S. Burdon, *Nature,* **120,** 584 (1927).

[9] R. K. Schofield, *Phil. Mag.*, [7] **1,** 641 (1926).

[10] See criticism of J. A. V. Butler, *Proc. Roy. Soc. (London),* **113A,** 594 (1927).

[11] M. E. Laing, J. W. McBain and E. W. Harrison, "Colloid Symposium Monograph," Vol. VI, **1928,** p. 63.

[12] W. D. Harkins and D. M. Gans, "Colloid Symposium Monograph," Vol. V, **1927,** p. 40; Vol. VI, **1928,** p. 36.

tained in connected apartments. Whenever a bubble entered the apparatus, it displaced its own volume of liquid into the next compartment and simultaneously from that to the next, and so on. Then as the bubble passed on to each successive compartment, that volume of solution necessarily returned to replace it. Since the liquid within each compartment was kept well stirred by the movement of the bubbles, each of the tens of thousands of bubbles passed in any one experiment acted as an efficient pump for mixing the initial impoverished solution with that from the middle compartments and the final enriched solution. The observed change was, therefore, necessarily far less than that which actually occurred. Even so it is remarkable that in nearly every case the results were far larger than those predicted. The simple expedient of allowing the bubbles to pass into a separate vessel before they collapse removes the possibility of loss by mixing.

It is seen from Table I that results for simple non-electrolytes, p-toluidine, camphor and amyl alcohol (confirmed by Harkins and by the present work), are far in excess of those possible according to the Gibbs equation. This discrepancy is not due to use of concentration in place of chemical potential in the Gibbs formula, for in the case of p-toluidine it makes no difference whether concentration or activity is used as the basis of the calculation.[13] Many further examples are adduced in the present paper.

The picture of the surface of an ordinary solution arrived at by McBain and Davies is that of a monomolecular surface layer of oriented molecules which serve as points of support for the growth of chains of oriented molecules relatively far into the solution, such chains being evanescent, being constantly broken up by thermal vibrations and as constantly replaced. It is very interesting that Sir William Hardy should have arrived independently at the same conclusion from quite other evidence.[14]

Measurements of the Adsorption at the Air–Solution Interface.—In the present work the method of McBain and Davies[1] was used to determine the adsorption at the air–solution interface of the following substances: phenol, p-toluidine, iso-amyl alcohol, resorcinol, thymol, acetic acid, butyric acid, caproic acid, nonylic acid and sodium chloride. The surface excess (or deficiency) of each of these substances was determined over a considerable concentration range and compared (a) with the amount predicted by application of the Gibbs equation both in the approximate and in the strict form and (b) with the amount required to complete a monomolecular surface layer both for vertical and for horizontal orientation of the adsorbed molecules. The surface tension and activity data were taken from the literature.

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[13] J. W. McBain, W. F. K. Wynne-Jones and F. H. Pollard, "Colloid Symposium Monograph," Vol. VI, 1928, p. 57.

[14] W. B. Hardy, J. Gen. *Physiol.*, **8**, 641 (1927).

Experimental Method

Gas bubbles were passed through an aqueous solution of the solute contained in a long, nearly horizontal glass tube of large diameter. The bubbles were caused to drain in a short vertical tube of smaller diameter and to pass over into and collapse in a descending portion of this tube. The liquid thus collected in a separate receiver contained not only the amount of solute to be found in an equal volume of the original solution but also the excess solute adsorbed on the surfaces of the bubbles. The absolute amount of this excess was determined by comparing the concentrations of collected liquid and original solution in a Zeiss interferometer. A number of values of Γ were determined successively in the course of a single experiment without interrupting the course of the bubbling. Nitrogen gas was used because of its inertness. The surface tension is considered to be the same as that at an air–solution interface.

The apparatus, shown diagrammatically in Fig. 1, consists essentially of a system S_1, S_2, S_3 for saturating the nitrogen, an "adsorption tube" CD ending in the short vertical draining tube EP and a receiver B_2.

Nitrogen from a cylinder equipped with a pressure regulator is freed from carbon dioxide present by passage through strong potassium hydroxide solution in the gas washing bottles A, A. From these it passes in a steady stream of bubbles through the saturators, S_1, S_2, S_3, where it comes into equilibrium with a solution of exactly the same concentration as that in the adsorption tube. Many blank tests of the effectiveness of this saturating system were made by bubbling gas through the apparatus in the ordinary way but keeping the liquid supply shut off so that all bubbles collapsed in the horizontal tube. In most cases no change in concentration was produced.

The mercury manometer M is connected as shown. The capillary tube K serves to regulate and steady the flow of gas through the rest of the apparatus.

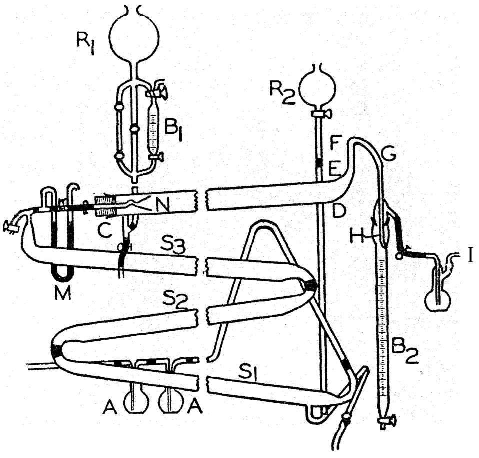

Fig. 1.—The adsorption apparatus.

A constant stream of bubbles of the same size is formed at the specially shaped bubbling nozzle N and passes slowly along the tube CD filled with a solution of the solute whose adsorption is to be determined. Here adsorption, if any, takes place at the surface of the bubbles. Each bubble finally rises through the tube EF, where it joins a column of nearly cylindrical, rapidly draining films, which are continually passing over the bend at F and being replaced from behind. The appearance of this column of films is shown in Fig. *2*. The time required for passage along the tube CD is about twelve seconds, for the tube EF about one and one-half seconds.

The films with their adsorbed surface layers collapse in the descending tube FGH, and the liquid from these collects in the receiver B_2, which is a 100-cc. buret attached to

GH by a ground-glass connection and equipped with a large-bore glass stopcock for rapid emptying. The nitrogen released by collapse of the bubbles leaves the apparatus at I and passes through a gas meter (Boys bell meter). The end of the tube GH was beveled and bent so as to touch the side of the buret. The effect of this detail was to cause the complete collapse of any films which had reached this orifice still unbroken. The end of the buret outlet was cut off close to the stopcock to reduce the amount of liquid remaining in this part.

The reservoirs, R_1 and R_2, are for supplying liquid to the adsorption and the saturating tubes, respectively. The means of emptying the apparatus are shown in the drawing.

DIMENSIONS OF THE APPARATUS

Tube	CD	EF	S_1, S_2, S_3
Inside diameter, cm.	2.5	0.86	1.8
Length, cm.	156	8	120
Slope, %	4–8	Vertical	8

Procedure

At the beginning of each new study the entire apparatus and all glassware to be used were cleaned thoroughly with hot H_2SO_4–$K_2Cr_2O_7$ mixture and rinsed repeatedly with distilled water. The aqueous solutions were made up in most cases with boiled out distilled water and a fresh solution was used for each experiment except in the first and the last few runs, in which cases the solution was carefully protected after use and remixed for the next experiments.

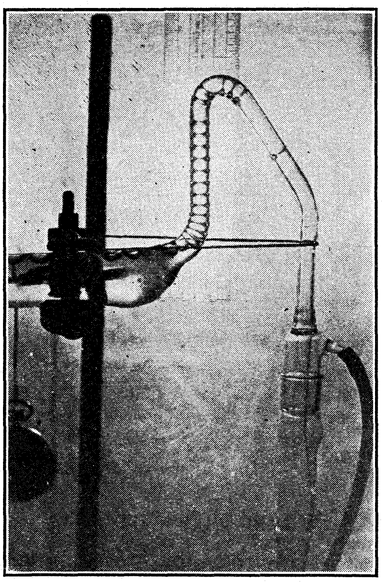

Fig. 2.—Detail of adsorption apparatus.

The adsorption apparatus and the collecting bottles were rinsed with the solution and the entire apparatus was filled. Bubbling was then started and the time noted. The bubble rate and the supply of liquid from reservoir R_1 were adjusted until a stable column of cylindrical films was formed in the draining tube EF and passed over unbroken into the descending tube FGH. During this time collapsed film liquid was allowed to run out of the buret and was not collected.

The adsorption experiment proper was started by closing the stopcock of the receiver-buret, and time and meter reading were noted. After any desired amount of liquid had collected in the receiver, the time was noted, the meter read and the collected liquid run out into a weighed, stoppered bottle. The collection of samples of collapsed film liquid was repeated as many times as desired in exactly the same way, and independent values of Γ were calculated from the separate sets of data. At the close of the run the liquid remaining in the adsorption tube was withdrawn and its concentration compared with that of the original solution. The total change in concentration (usually a loss) was distributed over the whole period of the run, and the observed concentration changes in the samples of collected film liquid were recalculated with reference to the mean concentration of the solution with which the bubbles were in contact at the time of collection.

Analysis of Solutions.—The analysis was made with a Zeiss interferometer for liquids. The following table shows the calibration equivalents for 1° determined in grams per cubic centimeter.

TABLE II

INTERBEROMETER CALIBRATION EQUIVALENTS[a]

	Value of 1 division in g./cc. X 10^6		
Substance	2-cm cell	4-cm. cell	8-cm. cell
Phenol	4.2	(2.0)	
p-Toluidine	3.18	1.54	(0.73)
Iso-amyl alcohol		3.93	1.91
Resorcinol		1.9	(0.91)
Thymol			1.14
Acetic acid		5.74	
Butyric acid		1.63	
Caproic acid		4.00	
Nonylic acid		2.18	
Sodium chloride		2.35	
Menthol			3.3

[a] Numbers in parentheses were calculated in each case by multiplying the actually determined calibration value for another cell (in terms of the same substance) by the ratio of the calibration values of these two cells for a different substance. For example, 1 division (4-cm. cell) = 2.0×10^{-6} g./cc. of phenol = $4.2 \times 10^{-6} \times 1.54/3.18$ (ratio from *p*-toluidine calibrations).

In the analysis great care was taken to ensure freedom from external contamination, to prevent evaporation changes and to secure uniformity of temperature—precautions especially necessary because the interference bands by which the comparisons are made are very easily distorted and shifted by small temperature inequalities in the solutions being measured and because the concentration changes observed were, at the most, very small relative to the total concentration of the solutions used.

Calculation of Results

The adsorption Γ is the absolute excess of solute transported on the bubble surfaces divided by the total adsorbing surface and is expressed in this paper in grams per square centimeter $\times 10^{-8}$.

$$\Gamma = \frac{1^\circ \times r \times V_c \times S_c^m}{2V_g + 2\pi r^3 B}$$

where V_c is the volume of solution collected, determined by weight, assuming unit density; S_c^m is the change in interferometer readings corrected with reference to the mean concentration of the solution during its collection; V_g is the volume of gas and B the number of bubbles passed during the collection of one complete sample. It is assumed that each bubble is a cylinder of radius 0.43 cm. At least 100 sq. cm. of bubble surface should pass over for each cubic centimeter of collapsed liquid collected; that is, the effective depth of the surface studied should not exceed 0.1 mm.

On account of the great difficulty of counting visually the number of bubbles when the rate was high (usually over 200 and frequently 300 to 400 a minute) an automatic, electrical apparatus was devised for the purpose (Fig. 3). By this means the total number of bubbles passing could be determined directly and with accuracy, and observations of duration and bubble rate were no longer necessary for the final calculation.

In Fig. 3 CB is a detail of the adsorption tube showing the bubbling nozzle equipped with a circuit breaking device which consisted of two platinum wires sealed into glass tubes on opposite sides of the nozzle and arranged so that the protruding tips of the wires extended vertically up into the path of the bubbles leaving the nozzle. As each bubble passed, the platinum points pierced it (without affecting its stability) and thus became separated by a non-conducting gaseous gap.

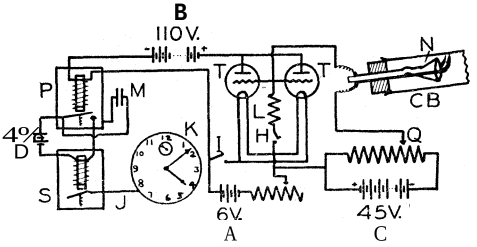

Fig. 3.—The electrical bubble counter.

The circuit breaker was inserted in the grid circuit of a three-electrode vacuum tube. Power amplifier tubes T,T were used of such characteristics that a normal plate current of about 30 milliamperes flowed when the plate voltage B was 110 volts, the filament voltage **A 6** volts and the grid voltage zero. By means of a voltage divider circuit Q connected to a 45-volt dry battery C the optimum (negative) voltage could be applied to the grid. The negative terminal of the C battery was connected through the circuit breaker to the grid (positive terminal to filament). The negative voltage thus applied reduced the plate current to zero, and because of the rectifying action of the tube no current flowed through the grid circuit and so *no electrolysis took place in the solution.*

When a bubble passed over the platinum points and broke the circuit, the grid charge was immediately dissipated through the grid leak I, (2 megohms), and the full current passed through the plate circuit of the tube. In order to double the amplification effect the two power tubes T,T were connected in parallel and their plate currents were fed through a single circuit.

A 150-ohm telegraph relay P was inserted in the plate circuit with suitable capacity across the points (2 mfd. condenser M). The secondary terminals of this relay were connected in series with a circuit composed of a 4-volt source of direct current D and a 20-ohm telegraph relay S.

A clock K was used as a mechanical counting device. After removal of hair spring and balance wheel the escapement lever was connected through J to the armature of relay S, whose movements therefore actuated the escape wheel movement. Two readings of the "apparent time," translated into seconds and multiplied by 2 (gear ratio of escape wheel to seconds wheel), gave the total number of bubbles which had passed during the interval.

The counter works best with solutions of low conductivity. When the conductivity becomes large, a conducting film of liquid is left on the surface of the platinum wires and the glass tubes during the passage of the bubble, and the grid circuit is thus continued down the outside of the wires and across the solution at the surface of the bubble.

Thymol C. P. from Coleman and Bell and Eastman caproic acid were used, Kahlbaum caproic acid being apparently less pure and giving a lower value. The other chemicals were the best obtainable from Kahlbaum. *p*-Toluidine was further purified by sublimation and this doubled the amount of sorption, making it the same as that found by McBain and Davies.

To save space the results are given only as points on the graph but each of these points is the mean of at least five and in many cases more experiments. The value of Γ for 3.0 g. of iso-amyl alcohol per liter is the mean of 129 measurements and is 11.0×10^{-8} as compared with the predicted Gibbs value 3.0×10^{-8}.

Negative adsorption was demonstrated in the experiments with aqueous sodium chloride, for which Harkins and McLaughlin[15] and Goard and Rideal[16] had simultaneously predicted from activity data a negative sorption approximately equivalent to the complete absence of sodium chloride from the first layer of water molecules on the surface. At first sight these experiments would seem to be impossible since stable bubbles or films will not rise from strong solutions of sodium chloride. However, it was discovered in experiments with caproic acid that with our apparatus it made very little difference to the results if the films were broken before

TABLE III

CROSS SECTIONS AND AREAS OF MOLECULES DEDUCED FROM LITERATURE ON THIN FILMS AND ON X-RAYS, AND HENCE THE AMOUNTS OF ADSORPTION PREDICTED FOR A CLOSE-PACKED MONOMOLECULAR LAYER

	Minimum area per molecule, Å.^{2}		Monomolecular adsorption, g./cm.^{2} $\times 10^8$	
Solute adsorbed	Vertical orientation	Horizontal orientation	Vertical orientation	Horizontal orientation
Amyl alcohol	21	39	6.7	7.4
Acetic acid	21	21	5.2	5.2
Butyric acid	21	32	6.9	4.5
Caproic acid	21	45	9.2	4.3
Nonylic acid	21	61	12.4	4.3
Phenol	24	39	6.5	3.9
p-Toluidine	24	45	7.4	3.9
Resorcinol	28	46	6.6	3.9
Thymol	38	..	6.6	...

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[15] W. D. Harkins and H. M. McLaughlin, THIS JOURNAL, 47, 2083 (1925).

[16] A. K. Goard and E. K. Rideal, *J. Chem. Soc.*, 127, 1668 (1925).

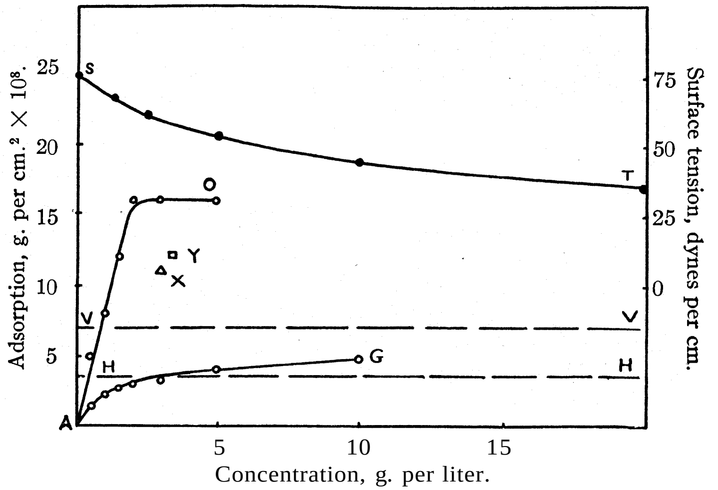

Fig. 4.—Adsorption of amyl alcohol. ST, Surface tension (15°) according to Edwards;[17] AO, adsorption observed by McBain and Davies;[1] X, adsorption observed by writers (mean of 129 measurements); Y, adsorption observed by Harkins and Gans;[12] AG, adsorption calculated (25°) by Gibbs concentration formula; VV, monomolecular adsorption (vertical orientation); HH, monomolecular adsorption (horizontal orientation).

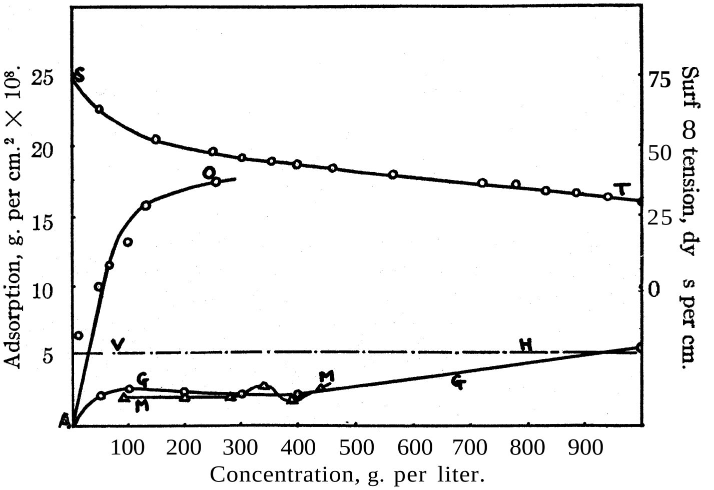

Fig. 5.—Adsorption of acetic acid. ST, surface tension according to Whatmough;[18] AO, adsorption observed; AGG, adsorption calculated by the Gibbs concentration formula (25°); MM, adsorption calculated by Milner[2] from same data and formula; VH, monomolecular adsorption (vertical or horizontal orientation).

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[17] P. R. Edwards, J. *Chem. Soc.*, 127, 744 (1925).

[18] W. H. Whatmough, *Z. physik.* Chem., 39, 129 (1902).

passing over the bend, provided that a steady flow of liquid slightly larger than usual was allowed to pass over continuously. Using this device the actual deficiency of salt in the liquid flowing over was four to eight times larger than that predicted by the Gibbs equation.

Comparison of **Observed,** "Gibbs" and Monomolecular Adsorption.—Inspection of the curves, Figs. 4 to 13, shows that the adsorption calculated from the approximate (concentration) Gibbs equation increases rapidly with concentration, attains a maximum while the solution is yet fairly dilute and the surface tension is still decreasing, and then drops in a way for which it would be difficult to account on a physical basis. The effect of using the exact equation involving activity, as is shown in the graphs, makes but little difference for the lower concentrations of the simple substances we have selected for study, but it frees the curves from the anomalous decrease in concentrated solutions.

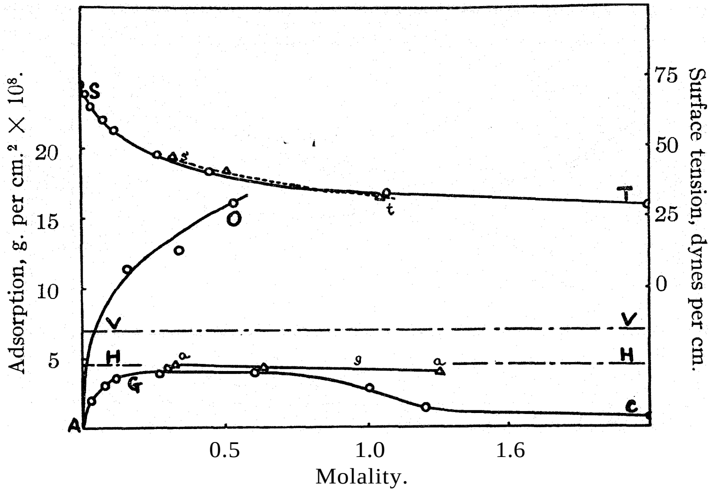

Fig 6.—Adsorption of butyric acid. ST, surface tension (25°), according to Drucker,[19] plotted against molality; ST, surface tension plotted against activity on same scale as molality; AO, adsorption observed; AGC, adsorption calculated *(25")* by Gibbs concentration formula; aga, adsorption calculated (25") by Gibbs activity formula (activity data from Rury);[20] VV, monomolecular adsorption (vertical orientation); HH, monomolecular adsorption (horizontal orientation).

It should be pointed out that "Gibbs" adsorption is not, as commonly supposed, necessarily identical with monomolecular adsorption, although the number of times the maximum "Gibbs" value approximates either one or the other of the monomolecular values is indeed suggestive of a physical reality for the calculated quantity which may be more than fortuitous.

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[19] K. Drucker, Z. *physik. Chem.,* 52, 641 (1905).

[20] C. R. Bury, *Phil.* Mag., [7] 4, 980 (1927).

However, the large number of experimental results obtained by McBain and Davies and in the present work indicate very strongly that the Gibbs equation does not supply real values. Of the ten substances investigated in this Laboratory, eight have been found to be adsorbed in amounts which are from two to eight times that predicted by the Gibbs theorem. The plotted curves show this very strikingly. A possible explanation of the relatively lower results obtained with thymol and nonylic acid is given below.

The amounts found to be adsorbed are from two to four times the quantities which could be accommodated in a monomolecular surface layer of vertically oriented molecules with even the closest packing ever observed in condensed films of related compounds. The adsorption effect must, therefore, extend beyond one molecular dimension and the results support McBain's suggestion[1] as to the structure of adsorbed layers at solution surfaces.

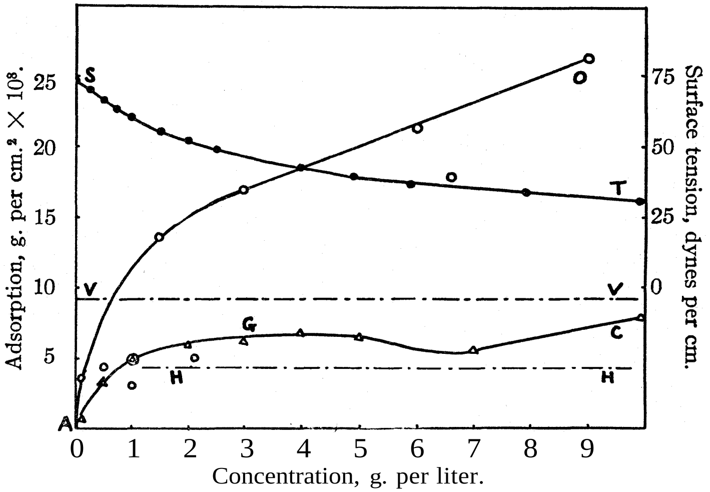

Fig. 7.—Adsorption of caproic acid. ST, surface tension (19°) according to Szyszkowski;[21] AO, adsorption observed; AGC, adsorption calculated (25°) by Gibbs concentration formula; W, monomolecular adsorption (vertical orientation); HH, monomolecular adsorption (horizontal orientation).

Discussion

These moving surfaces carry several times more solute than is compatible with the equation of Gibbs, and yet nearly all the experimental errors would seem to be operating so as to prevent the full real adsorption from being shown. Satisfactory blank tests have shown that the obvious experimental errors, such as incomplete saturation of the gas, have been

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[21] B. von Szyszkowski, *Z. physik. Chem.*, 64,385 (1908).

eliminated. The following effects would tend to counterbalance part of the true adsorption: (a) traces of contamination or impurity, such as a trace of grease from the stopcocks; (b) the frictional resistance to the movement of the cylindrical walls of the drained bubbles, as discussed by McBain and Davies (in the present work the ratio between radius and length was always between 0.6 and 1.0); (c) if the bubbles were spheres instead of true cylinders, all recorded results should be increased by 10%; (d) the shortness of time (about sixteen seconds) allowed for adsorption to occur; (e) the rubbing of the bubble against the liquid would tend to strip off the more loosely held molecules and chains so that the dynamic surface would sorb less than a motionless static one.

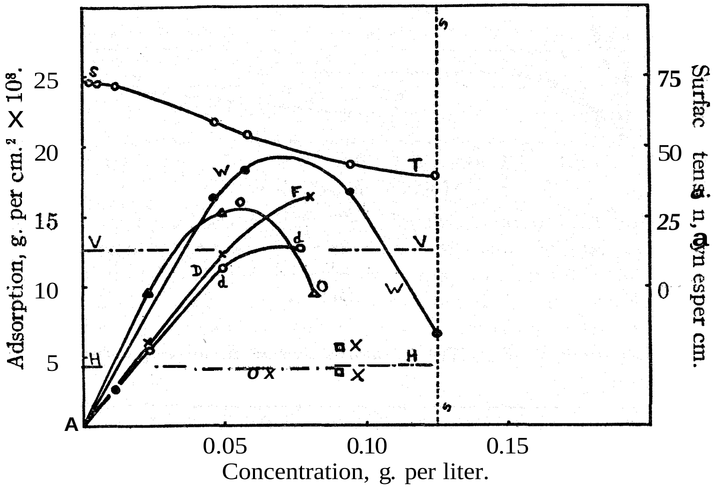

Fig. 8.—Adsorption of nonylic acid. ST, surface tension (18°) according to Forch;[22] AOO, adsorption observed by Donnan and Barker;[4] X, adsorption observed by the writers; ADF, adsorption calculated by Donnan and Barker by Gibbs concentration formula from Forch's S. T. data; Add, adsorption calculated by Donnan and Barker from own S. T. data; AWF, adsorption calculated by writers from Forch's S. T. data; VV, monomolecular adsorption (vertical orientation); HH, monomolecular adsorption (horizontal orientation); ss, saturated solution.

The ad *hoc* assumption has been made in several quarters that adsorption of the substances we have used is quick and desorption abnormally slow, although there is no evidence whatever for this assumption. The idea is that the moving bubble could thus accumulate an undue excess of material in its rear. However, closer examination of the processes of diffusion involved in adsorption renders this assumption less attractive. The extent of the Gibbs adsorption is entirely conditioned by the rate at which

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[22] C. Forch, *Wied. Ann.*, 68,801 (1899).

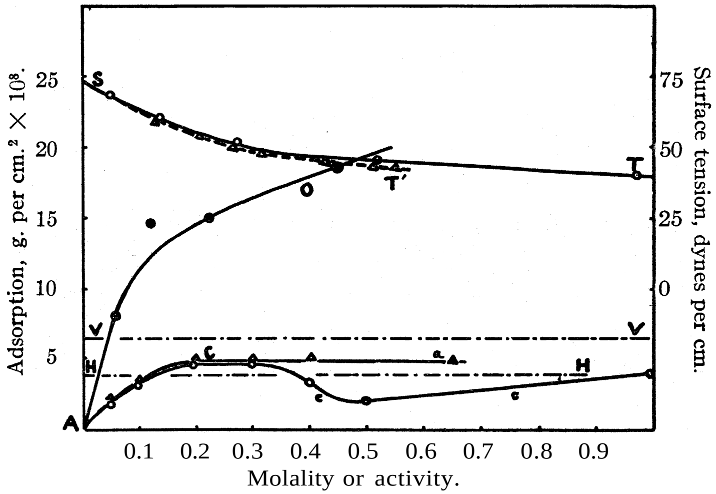

Fig. 9.—Adsorption of phenol. ST, surface tension plotted against molality, data of Goard and Rideal;[16] ST', surface tension plotted against activity, data of Jones and Bury;[23] AO, adsorption observed; ACa, adsorption calculated from activity formula; Acc, adsorption calculated from concentration formula; VV, monomolecular adsorption (vertical orientation); HH, monomolecular adsorption (horizontal orientation).

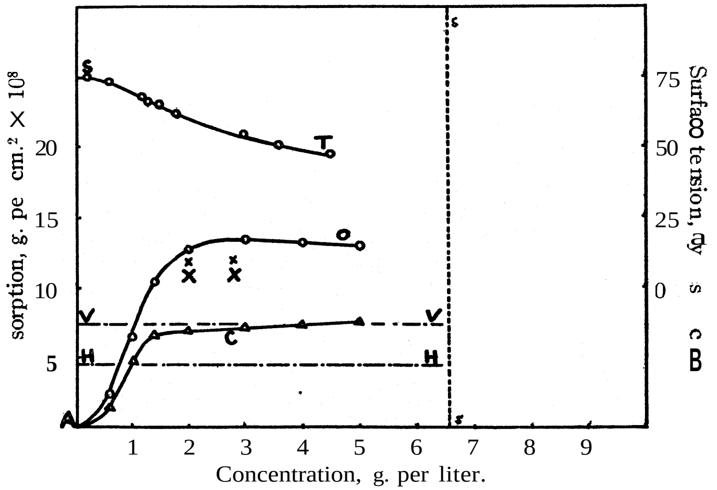

Fig. 10.—Adsorption of *p*-toluidine. ST, surface tension, according to Edwards;[17] AO, adsorption observed by McBain and Davies;[1] X, adsorption observed by writers; AC, adsorption calculated from concentration formula; VV, monomolecular adsorption (vertical orientation); HH, monomolecular adsorption (horizontal orientation); ss, saturated solution.

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[23] E. R. Jones and C. R. Bury, *Phil.* Mag., [7] 4,841 (1927).

the solute molecules diffuse into the depleted portions of the solution in more immediate contact with the bubble. An instantaneous adsorption would be zero adsorption according to the Gibbs definition. This

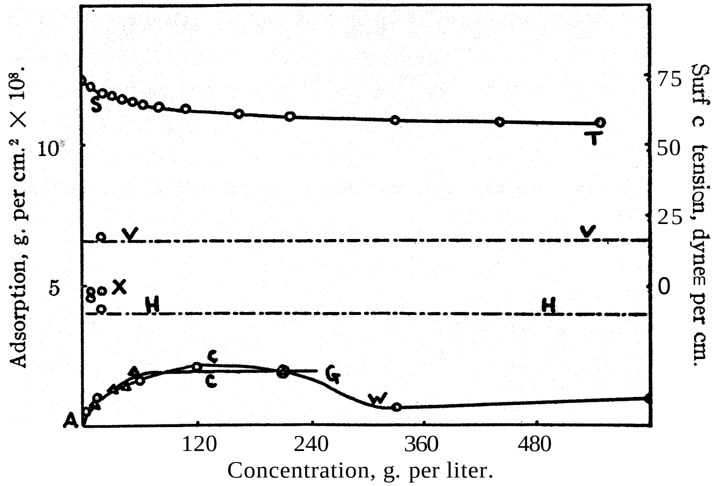

Fig. 11.—Adsorption of resorcinol. ST, surface tension according to Harkins and Grafton;[24] X, adsorption observed by the writers; ACW, adsorption calculated by the writers from the concentration formula; ACG, adsorption calculated by Harkins and Grafton.

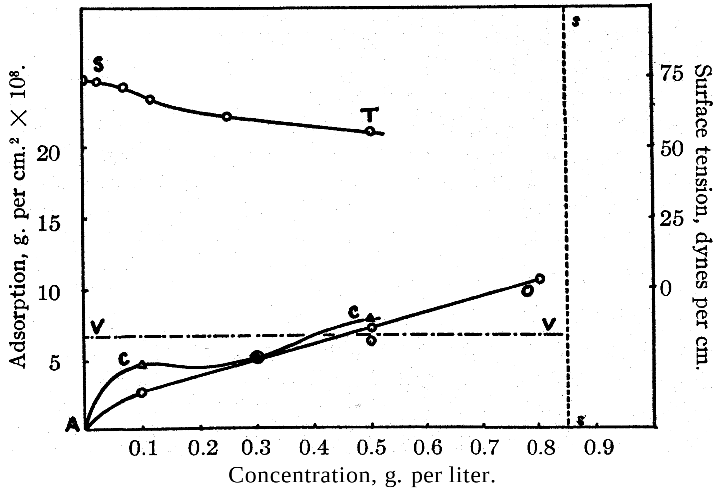

Fig. 12.—Adsorption of thymol. ST, surface tension, according to Edwards;'' AO, adsorption observed; ACC, adsorption calculated from concentration formula; ss, saturated solution; VV, monomolecular adsorption (vertical orientation).

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[24] W. D. Harkins and E. H. Grafton, This Journal, 47,1330 (1925).

diffusion rate is proportional to the difference in concentration between the solution in this region and that in the bulk phase. In very dilute solutions, in addition to smaller diffusion rate, the molecules have to diffuse from a far greater distance to supply the absolute amount of material adsorbed at the surface, and one would therefore expect low results with such solutions as those of thymol and nonylic acid. However, the practical effect of setting up the ad *hoc* assumption referred to is to discard all measurements made by the dynamic method, and there are no others that have been satisfactorily substantiated. The present custom of using the Gibbs theorem instead of experiment seems decidedly artificial.

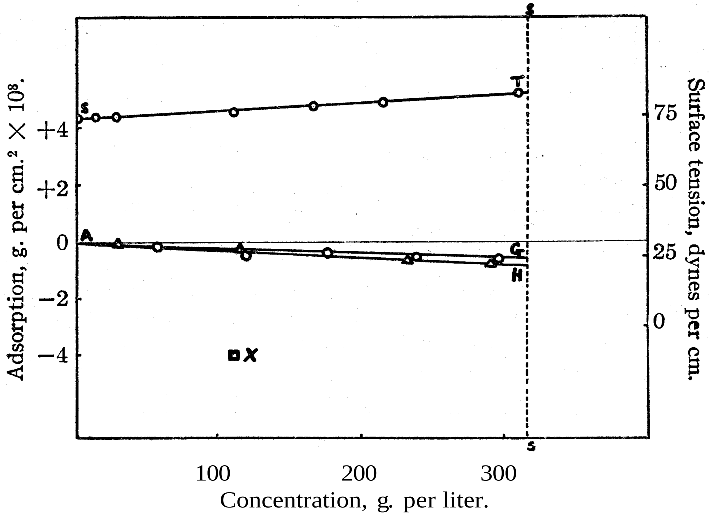

Fig. 13.—Negative adsorption of sodium chloride. ST, surface tension according to "International Critical Tables," Vol. IV, p. 465; AG, adsorption calculated by Goard[25] from the activity formula; AH, adsorption calculated from data of Harkins and McLaughlin[15] based on activities; X, adsorption observed; ss, saturated solution.

We are seeking a decision by the use of static surfaces, and the preliminary measurements with several substances indicate an even greater adsorption and therefore a greater discrepancy between experiment and either the treatment of Gibbs or the limited adsorption corresponding to a monomolecular film.

Further communications will deal with such experiments and with a discussion of the electrical terms ignored in the Gibbs equation.

Summary and Conclusions

1. The method of McBain and Davies has been used to measure the adsorption at the surface of solutions of *iso*-amyl alcohol, acetic, butyric,

[25] A. K. Goard, J. *Chem. Soc.*, 127, 2451 (1925).

caproic and nonylic acids, phenol, *p*-toluidine, resorcinol, thymol, camphor and sodium chloride.

2. When a bubble passes through a solution of a simple substance, it carries with it from 2 to 8 times as much of the solute as is predicted by the Gibbs adsorption theorem either in its exact or in its approximate form. The amounts carried are from 2 to 4 times that which can be accommodated in a monomolecular film of closely packed, vertically oriented molecules.

These findings fully substantiate those of McBain and Davies and support the views of McBain and of Hardy as to the constitution of surfaces of ordinary solutions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND OF STANFORD UNIVERSITY]

THE PHOTOCHEMICAL DECOMPOSITION OF BENZOQUINONE IN WATER AND IN ALCOHOL

BY PHILIP ALBERT LEIGHTON AND GEORGE SHANNON FORBES

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Parabenzoquinone, stable in the solid phase, can be photolyzed in alcohol or water solutions. In alcohol the products are acetaldehyde, hydroquinone and a third more complex product.[1] In water hydroquinone and a larger amount of the complex product are formed. Hartley and Leonard[2] found for the complex product approximately the formula of a dimer.

A similar photochemical decomposition of quinone in ether, glycerin, benzaldehyde, acetaldehyde, toluene, carbon tetrachloride and other solvents has been reported.[3]

Hartley and Little[4] made a qualitative study of the quinone photolysis, and a number of measurements of the absorption spectra of quinone solutions have been made[5,2] chiefly with reference to theories of the structure of the quinone "chromophore."

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[1] Ciamician and Silber, *Ber.*, 19, 2899 (1886); 34, 1530 (1901).

[2] Hartley and Leonard, *J. Chem. Soc.*, 95, 34 (1909).

[3] Ciamician and Silber, Ber., 35, 1080 (1902); 36, 1575, 4128 (1903); Klinger and Standke, *ibid.*, 24, 1340 (1891); Klinger, *ibid.*, 19, 1864 (1886); 24, 1340 (1891); Klinger and Kolvenbach, *ibid.*, 31, 1214 (1898).

[4] Hartley and Little, *Proc. Chem. Soc.*, 27, 137 (1911); *J. Chem. Soc.*, 99, 1079 (1911).

[5] Hartley, Dobbie and Lander, "British Association Report," 1902, p. 107; Hartley, *J. Chem. Soc.*, 95, 52 (1909); Baly and Stewart, *ibid.*, 89, 506 (1906); Purvis, *ibid.*, 123, 1841 (1923); Klingstedt, *Compt. rend.*, 176, 1550 (1923); Lifschitz and collaborators, *Rec. trav. chim.*, 43, 269, 403, 654 (1924); *Z. Physik*, 38, 61 (1926); Light, *Z. physik. Chem.*, 122, 414 (1926); Marchlewskii and Moroz, Bull. *soc. chim.*, 35, 473 (1924).

The absorption spectrum of quinone between 2000 and 6000 Å. consists of three bands or regions, which Light, from an analysis of the vapor spectrum, holds to be due to different electronic states of excitation.

Lifschitz, from a study of the effect of substitution on the absorption spectrum, attributes the visible band to electrons belonging to the central carbon atoms in the conjugated quinone ring, and the first ultraviolet band to electrons belonging to the oxygen atoms.

We have carried out a critical quantitative study of this photolysis, varying wave length and the several concentrations. A second paper will deal with the effect of temperature and of various substituents.

The light source was a quartz mercury vapor arc designed to combine as fully as possible the long life of large diameter arcs with the high intensity of the constricted arc.[6] The legs of an inverted U, 6 mm. in internal diameter, dipped into mercury reservoirs left open to the atmosphere. A 5-cm. capillary, nearly filled with an iron wire, attached to each arm of the U rendered oscillation negligible. The electrodes were water cooled, and by adjusting the relative heights of water and electrode surface, mercury transfer was neutralized. Running on 3 amperes at 12 volts per cm. the radiation flux could be kept constant within 1% by taking readings once an hour.

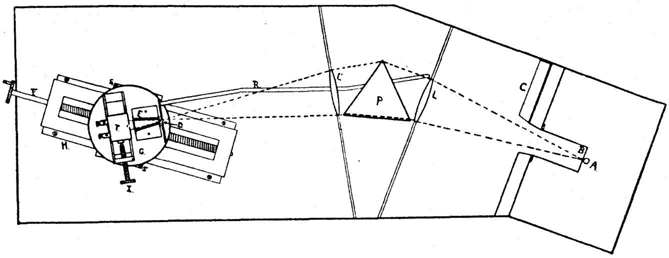

Fig. 1.—The monochromator.

The monochromator, illustrated by Fig. 1, included a fused quartz prism, P, 9.5 cm. along the base and 6.4 cm. high, and two fused quartz lenses, 6.4 cm. in diameter and 25 cm. in focus for λ3030 Å. The lamp A and collimating slit (1.2 by 30 mm.) were fixed with relation to the prism and lenses. The exit slit D (1 by 21.5 mm.) together with trapezoidal cell E and thermopile T were mounted on the table G which could be moved along the focal plane by the screw F and was kept perpendicular to the light beam by the pivoted rod R.

The energy fluxes normally obtained at the exit slit as it was moved along the focal plane were of the following order

Wavelength, mm.	1014	577	435	406	366	313	302	280	270	254
Intensity in ergs./sec. mm.^{2}	325	910	490	360	900	610	420	100	150	99

The thermopile, constructed by one of us, was of bismuth–silver, with 20 couples. The galvanometer, of sensitivity 14.6 mm. per microvolt, was mounted on a heavy Julius suspension. An energy flux of 1.00 erg./sec. mm.^{2} produced a deflection of 1.5 cm. on a scale 5 meters distant. Shunt and series combinations were necessary for many readings. The thermopile was calibrated with two standard carbon lamps

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[6] Forbes and Harrison, J. Opt. *Soc. Am.*, 11, 99 (1925); THIS JOURNAL, 47, 2449 (1925).

C39 and C40 certified by the Bureau of Standards. Experiments showed that the deflection obtained was not linearly proportional to the energy flux, and that it varied with the position of the mirror (that is, the portion of the scale covered). Accordingly, the galvanometer was adjusted so that the low or zero point of the swing always fell at or near the same point on the scale, and the calibration was extended to cover all possible deflections.[7] Three to five readings, using the ballistic method, were taken and averaged for each measurement.

The height of the focal plane slit, D, and the volume of liquid in the cell were so adjusted that the emergent beam as it fell on the thermopile was exactly the height of the sensitive column. Then by moving the thermopile across the beam by means of the screw I, taking readings at **2** mm. intervals, the entire beam was covered and the energy integrated as twice the sum of these readings ($2\Sigma B$) after the method of Villars devised in this Laboratory.[8] These values agreed to within 0.5% with those obtained by taking readings every mm. This method assumes that the thermopile itself integrates correctly the energy falling on it from top to bottom. The thermopile could be substituted for the cell when desired, in order to measure the relative incident intensity. By repeating this process at suitable intervals during an experiment, the integrals of the energy, incident and absorbed, could be built up.

Several absorption cells, differing in depth and volume, were used. They were covered to prevent evaporation, and so that oxygen could be excluded when desired.

In this reaction the photosensitive substance, quinone, is used up in known amount, with the formation of absorbing products. In addition, the solvent itself may absorb. The method devised takes account of these features.

The decomposition of quinone was followed by iodimetry, The calculation of the light absorbed by the undecomposed quinone was complicated through absorption by the solvent and also by the increase in strongly absorbing reaction products.

Ethyl alcohol was purified by the following steps: (1) allowed to stand over calcium oxide, then distilled; (2) 25 cc. of 12 N sulfuric acid added per liter of alcohol, the mixture refluxed several hours, then distilled; **(3)** 20 g. of potassium hydroxide and 10 g. of silver nitrate added per liter of alcohol, the mixture refluxed and distilled; (4) dried a second time over calcium oxide, this time being filtered before distillation. A one-centimeter layer of this alcohol transmitted 88% of λ2700.

Alcohol purified by addition of iodine[9] was found to fluoresce visibly in the shorter ultraviolet, so this method was not used.

The quinone used was purified by three successive sublimations, using the lowest possible temperature. Quinone was determined by the method of Valeur,[10] that is, adding an excess of hydriodic acid at 0° and titrating the liberated iodine with thiosulfate, using starch indicator, and excluding oxygen by bubbling carbon dioxide or nitrogen through the flask.

The quinone solution to be studied was made up fresh at the start of each experiment, and equal portions were pipetted into two similar cells, one of which was kept in the dark and the other exposed. At first the solution was stirred occasionally with a fine quartz rod during exposure. Later **a** mechanically driven stirrer was inrroduced, and all solutions were kept in an atmosphere of nitrogen at all times.

Integrations of emergent energy, $2\Sigma B$, and the corresponding relative incident intensity, ΣF, were made during each experiment on (a) cell plus water, (b) cell plus solvent, (c) cell plus solution before exposure and (d) cell plus solution after exposure.

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[7] G. S. Forbes, J. Phys. *Chem.*, 32,481 (1928).

[8] Villars, THIS JOURNAL, 49, 330 (1927).

[9] Henri and Castille, Bull. *soc. chim. biol.*, *6*, 299 (1924).

[10] Valeur, *Ann. Chem.*, 21,470 (1900).

Also, F readings were made at intervals during the exposure. The time which the solution was exposed in obtaining the energy readings was added to the time of the main exposure. The variation in intensity across the beam as well as from front to back of the cell makes necessary the unreserved assumption of the reciprocity law.

The corrections for reflection by the quartz faces were applied as in the work of Villars,[8] taking account both of the change in n with wave length and of the small deviation from normal incidence of the edges of the beam.

If we let $\Sigma F_{H_2O}/\Sigma B_{H_2O} = K$, it can be shown readily that the reflection correction cancels out and for any absorbing solution the fraction of the light transmitted, compared with the transmission of pure water as 1.00, is

$$L = \frac{\Sigma B_{\text{soln.}}}{\Sigma F_{\text{soln.}}} \times K \tag{1}$$

From the laws of Lambert and Beer it can be shown[11] that

$$Q = (1 - L)\frac{\log L - \log I}{\log L} \tag{2}$$

and

$$Q' = (1 - L')\frac{y(\log L - \log I)}{\log L'} \tag{3}$$

where Q and Q' are the calculated fraction of light absorbed by the quinone only, before and after the reaction, respectively; L and L' are as defined above for the solution before and after the reaction, respectively. As several different cells were used, these values cannot be compared without additional data not included here. I is the light transmitted by pure solvent compared with that transmitted by water as 1; y is the fraction of the original quinone remaining after the exposure.

Lacking a mathematical integration which would give the fraction, Q_m of the total incident energy of the exposure which was absorbed by the quinone alone, we found by experiment that

$$Q_m = \sqrt{QQ'} \tag{4}$$

very nearly. The total incident energy in ergs incident on the solution during the entire exposure is given by

$$E_{\text{total}} = \frac{2(\Sigma F_{\text{av}}S)}{(1 - r)K} \tag{5}$$

where ΣF_{av} is the average between each two successive F readings taken during exposure; S is the exposure in seconds between those same two readings; r is the fraction of the incident light reflected by a quartz wall (both faces).

In calculating ergs absorbed by the quinone from this, a small correction is made for the light reflected back into the solution from the rear face. The mean fraction so reflected is given nearly enough by $0.056 \times (L + L')/2$.

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[11] Luther and Weigert, *Z. physik. Chem.*, **53**, 408 (1905).

Assuming that the same fraction, Q_m, is absorbed as was absorbed in its first passage through the solution, we obtain

$$\text{Total ergs absorbed by quinone alone} = E_{\text{total}}\, Q_m\, [1 + 0.028(L + L')] \tag{6}$$

From this the photochemical efficiency

$$\Phi = \frac{\text{Molecules reduced}}{\text{Quanta absorbed}} = \frac{Nh\nu\ Vx}{1000Q_m\,[1 + 0.028\,(L + L')]E_{\text{total}}} \tag{7}$$

where V is volume of reaction mixture in cc., and x is molal concentration of quinone disappearing during exposure. Now setting A equal to the original molal concentration of quinone, i = absorption coefficient of solvent, q = absorption coefficient of quinone, \$ = absorption coefficient of products (all absorption coefficients given are exponents of the base ten), d = length of path of light beam in cell, in cm., and $E_{\text{total}} = E_0S$, where E_0 is incident intensity in ergs/sec. Equations 1–7 give the following general equation for @.

$$\Phi = \frac{Nh\nu\ Vx}{1000E_0Sq\sqrt{\dfrac{(1 - 10^{-(ic + qA)d})\,(1 - 10^{-(ic + q(A-x) + px)d})\,(A - x)A}{[ic + qA]\,[ic + q(A - x) + px]}}}$$

In the shorter wave lengths water itself becomes an appreciable absorbent.[12] This affects both absorption coefficients and absolute energy measurements. The absorption coefficients of quinone for those wave lengths were so much greater than those of water that the correction was inappreciable, but the absolute energy measurements, being taken as the light *transmitted* by pure water, were in error by the amount which the water absorbed. Accordingly, E_{total} was multiplied by the following factors, calculated from Kreusler's data

λ	1.06-cm. cell	8.27-cm. cell
2537	1.029	1.093
2700	1.025	1.078

Any hydroquinone formed by the reaction combines with more quinone to form quinhydrone. The method of calculating classes absorption by quinhydrone with that of the products and disregards the possible removal of quinone as quinhydrone. Assuming that quinone so removed is rendered completely inactive, that all the quinone reduced goes to form hydroquinone, and using the dissociation constant of Luther and Leubner[13] for quinhydrone, it is found that the calculated values for quantum efficiency would be from 1 to 5% too low, depending on the amount of quinone reduced.

We constructed a quartz spectrograph of 60 cm. focal length, and obtained upon each plate used spectrograms of the light transmitted by our absorption cells with and without solute. The characteristic curve of

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[12] Kreusler, *Ann. Physik*, 6,421 (1901).

[13] Luther and Leubner, J. *prakt.* Chem., 85,314 (1922).

each of these plates was derived from additional spectrograms made upon it with calibrated blackened wire screens in constant irregular motion. The plates were measured up by using a photometer similar to one described by Harriscn but constructed by us. We are grateful for valuable suggestions offered by Professor Harrison during the measurements. Absorption coefficients were in good agreement. The absorption coefficients of potassium nitrate solutions measured on our monochromator agreed within experimental errors with those obtained by von Halban and Ebert,[14] thus checking our procedure.

Experimental Results

1. Preliminary.—The velocity of the dark reaction is indicated by Table I. In alcohol solution, A3680 is much more strongly absorbed by the products than any other wave length. Addition of 5% hydroquinone actually decreased the absorption of λ3660 by about 2%, so the increase cannot be due to quinhydrone formation.

TABLE I

DARK REACTION

Time,	Relative oxidizing power			Time,	Light absorbed, %		
	In alcohol		In water		In alcohol		In water
min	25°	0°	25°	min.	A4350	λ3660	A3660
0	100	100	100	0	85	42	42
30	94	100	100	10	85	56	42
60	90	100	100	30	85.5	90	42
120	82	99	100	60	87	98	42
1440	..	..	100.5	120	88	100	42
			...	1500	97	...	50

TABLE II

TEMPERATURE COEFFICIENT OF DARK REACTION

	Period 20–30°
Calcd. from slope of dx/dt curve	2.8
Calcd. from k ior 1st order reaction	3.0
Calcd. from k for 2nd order reaction	2.9

Measurements of the dark reaction velocity were also made at 20 and 30°, and the temperature coefficient of the velocity calculated (Table II). Assuming $\Delta k_{10°} = 2.9$ for the interval 20–30°, the corresponding activation energy (using Arrhenius' equation) is 18,750 cal. This does not correspond to any of the vibrational periods in the band spectrum as analyzed by Light.[5]

The effects of dissolved substances on the reaction velocity are summarized in Table III. Oxygen retards the light reaction rate slightly in water, more in alcohol. Acids greatly retard the light reaction in water, but accelerate it slightly in alcohol. The dark reaction is much accelerated in alkaline solutions, but the light reaction is retarded.

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[14] Von Halban and Ebert, *Z. physik* Chem , 112,331 (1924).

TABLE III

EFFECT OF DISSOLVED SUBSTANCES

Dissolved substance	Percentage decomposed, time constant			
	Water in light	Alcohol In light	Alcohol In dark	Alcohol Difference
None (N_2)	27.0	29	0 8	28
Satd. O_2	24 5	17	6	16
0.012 *M* H_2SO_4	13 0	31	0	31
.012 M H_3PO_4		32	.5	32
012 M HCl	2 0	38	4 0	34
.012 M NaCl	8 0		..	
.012 M Na_2SO_4	21 0		..	..
012 M $NaC_2H_3O_2$		38	11 0	27
.012 M NaOH	..	81	70	11

As the products of the dark reaction absorb much of the light, it may be that the actual light reaction is not affected by alkali.

The data in Table IV indicate that quinone is the absorbent sensitive to light, and that the alcohol and the reaction products are "dark" absorbents; also that the reaction proceeds at a constant rate with respect to time.

TABLE IV

EXPERIMENTAL DATA

	Time, min.	Quinone concn., *N*	Alcohol, %	Percentage reduced by light
Quinone concn. changed	10	0 251	50	2.1
	10	.100	50	7.2
	10	020	50	15
	10	004	50	28
Alcohol concn. changed	10	016	3.3	26
	10	016	16.5	27
	10	016	33	29
	10	016	50	27
	10	016	65	25
	10	016	80	23
	10	016	98	21
Time changed	5	005	50	2.1
	10	005	50	4.2
	15	005	50	6.2
	20	005	50	8
	25	005	50	11
	30	005	50	13
	35	005	50	15

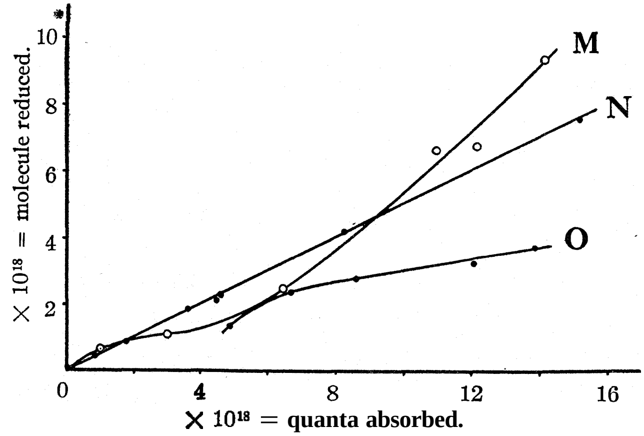
2. Quantitative Measurements in Pure Water.—See Table V and Graph 1. The presence of an induction period is indicated by Graph 1. The slope of the curves at any point represents the quantum efficiency, Φ, at that point. Removal of oxygen increases the reaction rate evenly over the entire range. One run only at 17° and one at 19°, compared with analogous runs at 25°, show a temperature coefficient of $\Delta k_{10^\circ} = 1.03 \pm 0.08$. This point is being further investigated.

Table V

Results in Pure Water (at 25° except as Noted)

A	Quinone concn.	Reduced, %	L	L'	Q_m	Molecules reduced × 10^{-18}	Quanta absorbed × 10^{-18}	Φ
4350	0.010	7.5	0.218	0.042	0.578	2.34	6.7	0.35
	.005	8.65	.495	.136	.374	1.35	4.9	.27
	.005	17.4	.500	.027	.281	2.72	8.6	.31
	.005	23.4	.500	.007	.224	3.65	13.9	.26
	.005	20.5	.500	.007	.226	3.20	12.1	.26
3660	.010	6.1	.460	.078	.375	1.93	3.5	.56
	.010	9.0	.416	.058	.405	2.84	5.0	.56
	.010	5.5	.452	.098	.402	1.71	3.9	.44
	.010	4.5	.500	.168	.392	1.42	3.2	.43
	.010	7.5	.470	.150	.404	2.28	3.3	.69
	.010	8.6	.448	.017	.312	2.70	8.1	.33
	.010	15.9	.460	.00025	.180	5.21	12.2	.43
	.010	25.2	.460	0	.125	7.85	15.4	.51
	.005	8.0	.664	.246	.260	1.25	2.3	.54
	.0025	9.6	.774	.541	.200	0.750	1.4	.55
	.0025	12.2	.812	.473	.156	.925	1.2	.77
	.0010	7.9	.911	.765	.0822	.246	0.44	.56
2700	.0010	10.0	.0239	.0091	.833	.308	0.57	.54
2537	.0050	4.3	...	..	.97	.67	1.22	.55
	.0025	0.85	...	..	.99	.066	0.10	.66
	.0025	1.4			.99	.109	0.30	.36
	.0025	3.15			.975	.245	0.65	.38
	.0025	8.5	...	..	.94	.663	1.10	.61
	.0025	12.0	...	..	.92	.93	1.42	.66
	.0010	9.4	...	..	.94	.30	0.49	.61

In one experiment the exposure was allowed to proceed long enough to have received the full effect of the inhibition, then interrupted for fifteen



M, water, λ2537; N, alcohol; O, water, λ4350.

Graph 1.—Comparison of reaction rate in water and alcohol.

hours and continued. The result was exactly the same as obtained with an uninterrupted exposure, showing that the cause of the inhibition is something inherent in the solution.

3. Quantitative Measurements in 50% Ethyl Alcohol.—Shown in Table VI. As indicated by Graph 1, the induction period found with water has disappeared. For all runs made in air the quantum efficiency decreases as the percentage of quinone reduced increases, and it becomes necessary to extrapolate back to zero reduction to get a true value of Φ. When oxygen was excluded, Φ was within limits of error independent of the amount reduced. The efficiency is also independent, within the range measured, of the original quinone concentration, and for wave lengths from 4350 to 2537 Å., independent of the wave length. Over this region Φ (extrapolated back to zero reaction for those experiments in air) averages, within limits of error, very close to 0.50. A definite threshold region is indicated by the decrease in efficiency above 4350 Å.

TABLE VI

RESULTS IN 50% ETHYL ALCOHOL (AT 25°)

λ	*Quinone* concn.	*Reduced,* %	L	*L'*	Q_m	*Molecules reduced*	Quanta absorbed $\times 10^{-18}$	Atm.	Φ
5770	0.010	2.4	0.528	0.561	0.401	8.6×10^{17}	1 9 0	**Air**	0.045
5460	.010	7.2	.385	.363	.598	1.36×10^{18}	6 93	N_2	.20
4350	.010	10.8	.149	.095	.734	3.37×10^{18}	6.94	**Air**	.49
	.010	16.2	.145	.033	.612	5.05×10^{18}	14 8	**Air**	.34
	.010	28.7	.145	.028	.558	8.95×10^{18}	29.7	**Air**	.30
	.005	14.0	.277	.170	.599	2.18×10^{18}	4.84	**Air**	.45
	.005	18.6	.420	.325	.496	2.90×10^{18}	6.11	**Air**	.48
	.005	20.5	.477	.413	.464	3.92×10^{18}	7.68	N_2	.51
	.005	29.0	.200	.144	.698	4.53×10^{18}	9.30	**Air**	.49
	.025	12.1	.598	.566	.354	0.94×10^{18}	1.85	**Air**	.51
	.025	21.1	.618	.542	.312	1.65×10^{18}	3.64	**Air**	.45
	.025	43.5	.594	.448	.273	3.39×10^{18}	10.66	**Air**	.37
	.001	8.0	.762	.774	.170	0.188×10^{18}	0.386	**Air**	.49
	.001	9.4	.799	.765	.168	0.293×10^{18}	0.651	**Air**	.45
3130	.005	6.5	.0151	.0125	.932	0.985×10^{18}	1.97	N_2	.50
	.005	8.1	...	...	.92	0.75×10^{18}	1.53	**Air**	.49
	.005	27.6	.0172	.0077	.77	4.18×10^{18}	8.68	N_2	.48
	.0025	15.2	.0038	.00175	.84	1.35×10^{18}	3.5	**Air**	.39
3020	.010	8.0	.00072	.00018	.86	3.1×10^{18}	6.5	**Air**	.48
	.005	3.0	.0010	.0004	.91	0.54×10^{18}	1.4	Air	.39
2700	.010	3.7	.0034	.0020	.90	1.4×10^{18}	2.35	**Air**	.60
2537	.005	4.3	...	...	.98	0.77×10^{18}	1.40	N_2	.55

4. Quantitative Measurements in Absolute Ethyl Alcohol.— Shown in Table VII. All were made in an atmosphere of nitrogen. As with 50% alcohol, the quantum efficiency is independent of wave length below λ4350 Å. The average for this region is 0.49. It drops off in λ5460, exactly as in 50% alcohol. The probable error of a single determination is ±0.05.

TABLE VII

RESULTS IN 100% ETHYL ALCOHOL (AT 23° EXCEPT AS NOTED)

Quinone concn , 0.005 M. Oxygen excluded

λ	Reduced, %	L	L'	Q_m	Molecules reduced $\times 10^{-18}$	Quanta absorbed $\times 10^{-18}$	Φ
5460	6 5	0 377	0 330	0 598	1 24	5 40	0.230
4350	4 6	552	483	438	0 879	1 88	.467
	11 6	593	541	446	2 22	4 98	.446
3660	2 4	845	709	152	0 458	0 842	.544
	11 2	790	429	178	2 15	4 21	510
3130	9 6	0031	0017	904	1 83	3 65	.502
2700	4 6	0085	00735	930	0 879	1 85	.475
	21 6	00848	00370	793	4 13	8 29	598

Discussion

The reaction in water differs from the reaction in alcohol. In water, at the start, when the inhibitive effect is a maximum, light produces little reduction of the quinone, yet the absorption coefficient of the solution increases sharply, showing that some change, not detectable by our method of analysis, is occurring.[2] The increase in absorption during the induction may be due to formation of the dimer postulated by Hartley and Leonard.[2]

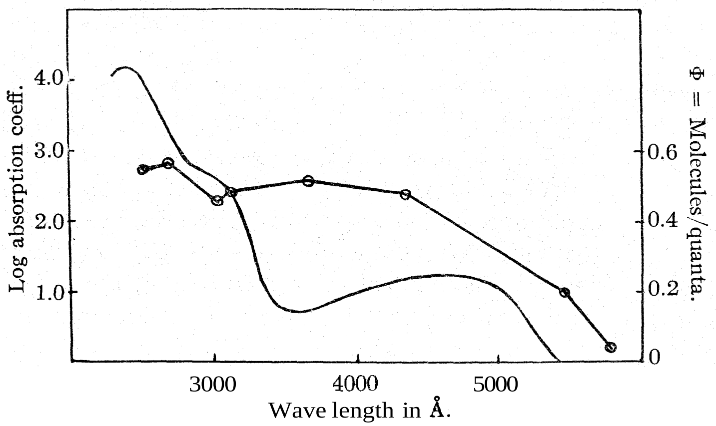
Beyond the induction period, the efficiency, as indicated by the slopes in Graph 1, becomes constant at about 0.16 for λ4350 and 0.9 for λ3660 and 2537. This indicates either a change in efficiency with wave length or else a threshold between λ3660 and 4350. In alcohol solutions the threshold is definitely between λ4350 and 5460, that is, it is displaced toward longer wave lengths by addition of alcohol.

In this regard, Light,[5] in the vapor spectrum, observed a disappearance of fine structure at about λ3100, which is in the second absorption band (attributed to oxygen electrons). According to the ideas developed by Henri this indicates a predissociation or activation which in the presence of a suitable acceptor can produce photochemical reaction. In both water and alcohol solutions, the point at which the molecule becomes sufficiently activated to react is displaced toward longer wave lengths, in fact, into the first absorption band. Light's measurements indicate an incipient disappearance of fine structure at about λ4500 in the first absorption band, which apparently corresponds with the photochemical threshold in alcohol solutions.

It becomes of interest to compare the photochemical efficiency at different wave lengths with the absorption spectrum in absolute alcohol,[5] (Graph 2). The threshold is clearly inside the first absorption band. The efficiency reaches its constant value (within limits of error) at λ4350 *and* remains *at this value into and clear through the second absorption band.*

These two bands probably represent absorption in two parts of the molecule, certainly two different electronic excited states, yet the quantum efficiency of the reaction produced is the same throughout.

The value of 0.5 for the efficiency recalls Weigert's[15] explanation of the same yield for nitrobenzaldehyde as due to the necessity for a groper orientation of the molecule with respect to the incident light before an effective absorption is produced. This explanation can be applied to quinone if one assumes the superoxide formula.



Graph 2.

However, the results can be explained equally well by assuming that every absorbed quantum is effective in producing activation, and that a 50% efficient secondary reaction is responsible for the observed yields. The quantum efficiencies in water solution, and the effect of dissolved substances on reaction rate, favor this latter explanation.

Summary

The photochemical decomposition of benzoquinone in water and alcohol solutions has been quantitatively investigated.

The reaction in water, as measured by amount of quinone reduced, shows an induction period, which disappears in alcohol solutions.

Evidence is shown of a threshold in the first absorption band, lying toward longer wave lengths in alcohol, toward shorter in water. Inside the threshold the photochemical efficiency is independent of wave length throughout the remainder of the first and the whole of the second absorption bands.

In alcohol the efficiency is independent of quinone concentration, and averages 0.5 at 25°. The temperature coefficient, $\Delta k_{10°}$, is near unity for the reaction in water.

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[15] Weigert and Brodmann, *Trans. Faraday Soc.*, **21,453** (1925).

NOTE

Apparatus for Determination of Moisture Content of Solids and the Sorption of Gases and Vapors by Solids at Elevated Temperatures.—In the course of an investigation conducted by the writer it was desirable to determine not only the water content but the quantity of water vapor sorbed by a solid, granular substance from various steam–air mixtures at temperatures from 100 to 450°. The apparatus developed for this purpose was unique in several respects and, although requiring the services of a skilled glass blower, may find application in work of a similar nature by others.

The apparatus, shown in the accompanying sketch, consists essentially of a constant-temperature vapor-bath B with liquid boiling under automatically controlled reduced pressure,[1] an air-bath M and a detachable weighing tube D. The construction of the apparatus will be apparent from a description of the procedure in determining, for example, the sorption of water vapor. The method consists in passing a steam–air mixture[2] over a weighed amount of the solid material at constant temperature until equilibrium is established, as evidenced by no further increase in weight. The steam–air mixture enters the air-bath tube M, which is covered by the ground glass cap F, through the preheating coil J. The glass stopper G hanging from the hook on the glass rod H, allows the gases to escape through the tube D containing the granular material and thence out through the ground-glass joint E which also serves as a support for the tube D. The tube M is sealed at I, to the inner tube N of the vapor-bath so that the entire cap F is about two inches below the top of the vapor-bath. The vapor from the boiling liquid[3] in B then fills the annular space between the outer wall of B and the inner tube N, thus maintaining the cap at the bath temperature. The temperature of the system may be read from the mercury thermometer suspended in the vapor-bath from the ground-glass stopper as shown. The outlet tube above the cap is wound with nichrome wire and heated electrically to prevent condensation of steam. A loose plug of glass or cotton wool in the open end of N excludes air currents cooling the cap F.

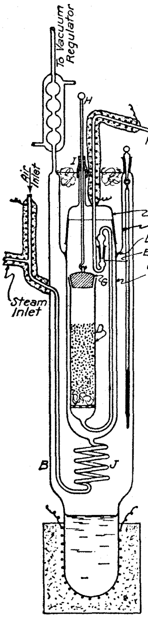

Fig. 1.

The experiment may be interrupted at any time for the purpose of weigh-

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[1] For description of automatic control device see Kuentzel, THIS JOURNAL, 51, 3347 (1929).

[2] See Kuentzel, "The Preferential Catalytic Oxidation of Carbon Monoxide in the Presence of Hydrogen," Part I, for description of a suitable steam generator.

[3] A list of suitable liquids and their boiling points is given in "International Critical Tables." 1926, Vol. I, p. 66.

ing by sliding the rod H through the rubber connector I, thus closing the stopper G. The tube K is then closed by a short rubber tube and glass bead and the entire sorption tube and cap ensemble removed and placed in a desiccator to cool. A vacuum type desiccator carrying a bottle neck in its cover enables one to insert the weighing tube into the desiccator in a vertical position. A thin rubber sleeve attached to the bottle neck, into which the cap F fits, then seals the desiccator. When cool, the small tube D is detached at the ground joint E for weighing. A correction must, of course, be made for the steam that condenses in the free space of the tube upon cooling.

When the apparatus is used for determining the moisture content of solid materials, the steam generator is cut off and a stream of completely dried air or nitrogen passed over the material in D. The effluent gases are then passed through a series of weighed drying tubes attached at K to collect the moisture. The loss in weight of the material in D serves as a check. The dissociation of moist materials which decompose upon heating with evolution of gases not absorbable by the drying agents used may thus readily be obtained by determining the total loss in weight of the material itself as well as the amount of water vapor evolved. The ability to interrupt the experiment easily and to determine the change in weight also enables one to follow the *rate* of sorption, drying or dissociation quite readily.

CONTRIBUTION FROM
FERTILIZER AND FIXED NITROGEN INVESTIGATIONS
BUREAU OF CHEMISTRY AND SOILS
DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
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RECEIVED JUNE 12, 1929
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[CONTRIBUTION PROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF HYDROCARBONS: ISOBUTYLENE[1]

BY CHARLES D. HURD[2] AND L. U. SPENCE[3]

RECEIVED MAY 20, 1929 PUBLISHED DECEMBER 11, 1929

In the first paper[4] of this series, data were recorded for the pyrolysis of n-butane and isobutane. The present paper concerns itself with *iso*-butylene, a hydrocarbon which possesses a branched chain of four carbons,

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[1] This paper contains results obtained in an investigation on "The Non-Catalytic Thermal Decomposition of Pure Hydrocarbons and Related Compounds," listed as Project No. 18 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project No. 18.

[3] American Petroleum Institute Junior Research Fellow.

[4] Hurd and Spence, THIS JOURNAL, 51,3353 (1929).

as does isobutane. It will be shown that isobutylene is much more stable than isobutane under similar conditions. Undoubtedly this observation is connected in some way with the greater or lesser "electron attraction" of the various radicals concerned. It leads to the inference that the carbon-to-carbon single bond in isobutane undergoes scission more readily than the similar single bond in isobutylene.

The literature furnishes no record of a quantitative study of the pyrolysis of isobutylene. Previous workers, however, have identified some of the products formed when this hydrocarbon is decomposed. A. A. Noyes[5] passed isobutylene through a glass tube heated to "low redness," and identified ethylene, propylene, butadiene, methane, hydrogen, benzene, toluene and naphthalene. Nef[6] found propylene, methane, hydrogen and a "small yield" of yellow oil as the decomposition products of *tert.*-butyl alcohol. Presumably isobutylene was an intermediate product. Ipatiev[7] reported that when isobutylene was passed over alumina at 500°, or over zinc chloride at 600°, there was no change into the isomeric butenes, but that some propylene, hydrogen and methane were formed.

Experimental

Isobutylene was prepared by refluxing 400 cc. (4.3 moles) of *tert.*-butyl alcohol with 150 g. (1.2 moles) of oxalic acid dihydrate. The gas evolved was collected and stored over water in a gasholder of 56-liter capacity. The yields of several runs averaged 80–90%. The only impurities in the gas were small quantities of air and the vapors of *tert.*-butyl alcohol. Before passing into the reaction tube, the gas was conducted through a wet test meter and then freed from water and alcohol vapors by a calcium chloride tower. A flowmeter was used for adjusting the flow of gas through the apparatus to a constant rate.

The reaction chamber was of pyrex tubing (2.5 × 90 cm.). It was heated in an electric tube furnace over 76 cm. of its length. The temperature was recorded and controlled accurately by a Leeds–Northrup potentiometer controller, as has been described in the first paper of this series. The volume of the heated portion was approximately 360 cc. and the inside surface was 600 sq. cm. To facilitate the removal of liquid products, the tube was placed vertically. Such liquids were condensed and removed from the escaping gases by passage through two U-tubes filled with glass wool and cooled to 0–5°. The effluent gases were measured by a second wet test meter. A sample of the gaseous products was removed for analysis toward the end of each run. For each experiment, 20–30 liters of *iso*-butylene was employed. A sketch of the apparatus is given in Fig. 1.

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[5] Noyes, *Mass. Inst. Tech. Quarterly*, *1*, 278–281 (1888).

[6] Nef, *Ann.*, **318**, 24, 25, 210 (1901).

[7] Ipatiev, *Ber.*, ***36***, 2008 (1903).

The gaseous products were analyzed by the absorption methods which were developed for the work on the butanes. The same sequence and the same precautions were observed. Mercury was used as the confining liquid in the Orsat buret. This work showed that the chief unsaturated hydrocarbons in the effluent gas were isobutylene and propylene (or allene), with a small amount of ethylene and acetylene.

A check on the values for the unsaturated hydrocarbons was obtained in a separate run by converting them into the bromides and then separating these bromides. The proportion of isobutylene and propylene as estimated in this manner agreed closely with the amounts found by gas analysis. The allene content was shown to be very small. Since the fuming sulfuric acid pipet should remove not only ethylene but also benzene and toluene vapors, it was to be expected that the ethylene bromide value for ethylene should be somewhat lower than the absorption value. Such was the case.

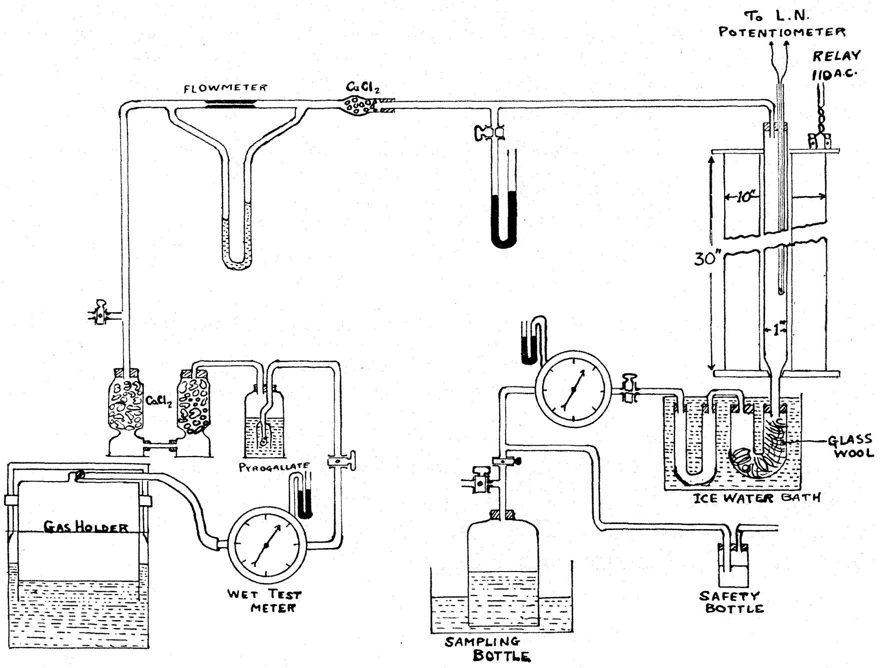

Fig. 1.

The decomposition was quite slow at 600°, but the rate increased rapidly with the temperature. In Table I is shown the amount of decomposition of isobutylene (97–99% purity) at the different temperatures used.

The rate of disappearance of the isobutylene was unchanged by dilution of the entering gas with nitrogen or with hydrogen (Table II). The rate of decomposition is therefore independent of the concentration.

TABLE I

DECOMPOSITION RESULTS

Temp., °C.	Contact time, sec.	Decompn., %	Temp., °C.	Contact time, sec.	Decompn., %
599	18	1.2	700	12	30.2
599	200	20.0	700	18	47.7
			700	23	54.0
652	18	11.1	700	25	51.4
652	27	22.7	700	32	64.3

TABLE II

DILUTION WITH NITROGEN

Temp., °C.	Contact time, sec.	Composition of entering gases Percentage by volume C_4H_8	N_2	O_2	Percentage decomposition
702	23	98.0	1.6	0.4	54.0
704	21	54.8	44.9	0.3	54.4

DILUTION WITH HYDROGEN[a]

Temp., °C.	Contact time, sec.	C_4H_4	Air	H_2	Percentage decomposition
702	23	98.0	2.0	...	54.0
704	22	51.8	3.7	44.5	56.8

[a] Although the extent of decomposition of isobutylene was not appreciably altered by the presence of hydrogen, still this gas was not an "inert" diluent. It was found that 62 cc. of hydrogen disappeared per liter of isobutylene decomposed, while the decomposition without the previous addition of hydrogen produced 265 cc. of hydrogen per liter of isobutylene decomposed. The disappearance of this hydrogen was accompanied by an increase in the methane content to the extent of 205 cc. per liter of *iso*butylene decomposed.

When the surface of the reaction tube was increased to twice its original value by packing the tube with small pyrex tubing, the rate of decomposition was also unchanged. This is revealed in Table III. The decomposition is, therefore, homogeneous or largely so.

TABLE III

EFFECT OF INCREASED SURFACE

Temp., °C.	Contact time, sec.	Vol. of tube, cc.	Surface, sq. cm.	Decomp., %
702	23	360	600	54.0
704	21	345	1200	51.8

Since the decomposition of isobutylene is independent of the concentration of the gas and is unaffected by an increase of surface, the reaction is unimolecular. The rate of decomposition should be given by the equation

$$\frac{dx}{dt} = k(a - x)$$

which, on integration, becomes

$$k = \frac{1}{t}\log_e \frac{a}{(a - x)}$$

In this equation a represents the original concentration of *iso*butylene, $(a - x)$ the concentration remaining after t seconds, and k the specific reaction rate. In the calculation of the values of k, given in Table IV, the concentrations of isobutylene have been expressed in moles per 22.4 liters at 0° and 760 mm.

TABLE IV

RESULTS OF EXPERIMENTS

Temp., °C.	Time, sec.	Concn. in moles per 22.4 liters Start	Finish*	k	Mean *k*
600	200	0.940	0.690	0.0016	0.0016
650	13	.990	.900	.0073	
650	27	.970	.762	.0089	.0081
700	12	.980	.634	.0362	
700	18	.975	.433	.0451	
700	22	.978	.294	.0547	
700	23	.980	.387	.0405	
700	25	.978	.380	.0378	
700	32	.983	.266	.0409	
N_2 700	21	.548	.212	.0451	
H_2 700	22	.518	.206	.0420	
700[b]	21	.978	.399	.0428	.043

[a] The final concentrations are somewhat in error, since the liquid products were removed before measuring the volume of the exit gases. Therefore, the concentration of the isobutylene at the end of the reaction was actually less than the figures in Table IV.

[b] Experiment with increased surface.

The heat of activation was calculated from the change in the specific reaction rate with the temperature, by means of the equation of Arrhenius

$$\frac{d(\log_e k)}{dT} = \frac{A}{RT^2}$$

wherein k is the specific reaction rate; T, the absolute temperature; R, the gas constant in calories; and A, the heat of activation. The mean values of k for the temperature of 600, 650 and 700° were used in these calculations.

Mean temperature, °C.	625	650	675
Heat of activ., *A*, cal./mole	52,700	55,700	59,100

A summary of the data of several experiments on the pyrolysis of *iso*-butylene at 600–700" under varying conditions are arranged in Tables V and VA. In Expt. 12 the olefin was diluted with nitrogen; in No. 13, it was diluted with hydrogen. Experiment No. 15 was an increased surface experiment such as has been mentioned above. In the other 700" experiments it will be seen that for each mole of isobutylene decomposed, 1.3–1.5 moles of other gases was formed with an exposure of from twelve to thirty-two seconds. Methane comprised about half of the gaseous portion, but since liquid products were found to be formed to the extent of 41–63% of the weight of *iso*butylene decomposed, it is apparent that methane formation is not the exclusive major reaction. In the various 700" experiments, methane represented 46–55% of the gases exclusive of the unchanged *iso*-

butylene. Five of the six results showed the hydrogen content to be 19–20%, and the sixth dropped to 14%. In general, therefore, hydrogen comprised about one-fifth of the gases. Propylene represented one-seventh or less (14–17%), and other gases were present in lesser amounts. Expressed somewhat differently, each 100 moles of isobutylene undergoing decomposition under these conditions gave rise to 59–83 moles of methane, 20–30 moles of hydrogen, 20–25 moles of propylene, lesser amounts of isobutane and ethylene and almost negligible quantities of acetylene.

The Nature of the Unsaturated Hydrocarbons Formed at 700°.—In a separate experiment isobutylene was decomposed at 700° at a contact time of nineteen seconds. The unsaturated hydrocarbons in the off-gas were analyzed by the bromide method to serve as a check on the absorption method of analysis. The gaseous products were dried with calcium chloride, and were then absorbed in bromine in dry carbon tetrachloride solu-

TABLE V

THE PYROLYSIS OF *Iso*BUTYLENE

Experiment	1	2	10	11	7	4	9
Temperature, °C.	599	599	652	652	700	700	700
Contact time, sec.	200	18	27	13	12	18	19
Entering flow, cc./min.	35	420	256	522	536	330	300
Exit flow, 25°, cc./min.	38	420	252	509	578	388	363
Press. in tube, mm. of Hg	750	747	744	743	755	744	720
Concn. of isobutylene in the entering gas, % by vol.	94	96.5	97	99	98	97.5	97
Decomposition, %	20	1.2	22.7	11.1	30.2	47.7	
Oil formation (% by weight of entering isobutylene)	...	...	9	7	14.1	30	23.3
GASEOUS PRODUCTS FORMED PER LITER OF ISOBUTYLENE ENTERING							
Propylene, cc.	61	4	39	16	66	109	...
Methane, cc.	118	...	65	15	177	312	...
Isobutane, cc.	54	...	40	22	40	29	...
Hydrogen, cc.	35	...	34	6	73	124	...
Acetylene, cc.	3	3	8	12	13	28	...
Oxides of carbon, cc.	7	4	10	9	12	6	...
Ethylene and aromatics, cc.	18	2	7	11	20	32	...
GASEOUS PRODUCTS FORMED PER LITER OF ISOBUTYLENE DECOMPOSED							
Propylene, cc.	305	...	172	144	218	228	...
Methane, cc.	590		286	135	586	655	
Isobutane, cc.	270		176	198	133	61	
Hydrogen, cc.	175		150	54	242	260	
Acetylene, cc.	15		35	108	43	59	
Ethylene and aromatics, cc.	90		31	99	66	69	
OIL FORMATION							
Yield of oil based on the weight of *iso*butylene dec., %	...	...	39.6	63	46.6	63	.

TABLE VA

THE PYROLYSIS OF *Iso*BUTYLENE

Experiment	14	6	5	8	12	13	15
Temperature, °C.	702	702	760	700	704	704	704
Contact time, sec.	22	23	25	32	21	22	21
Entering flow, cc./min.	261	258	236	172	281	284	270
Exit flow, 25°, cc./min.	322	308	296	226	331	309	320
Press. in tube, mm. of Hg	747	747	743	739	745	748	748
Composition of entering gas, percentage hy volume							
Isobutylene	978	980	978	983	548	51.8	37.8
Nitrogen	1.7	1.6	2.0	1 5	449	3 5	1.7
Oxygen	0 5	0 4	0 2	0 2	0 3	0.3	0 5
Hydrogen		. .	. . .	. .	. .	44 5	. . .
Percentage decomp.	627	540	514	643	544	568	51.8
Oil formation (% by weight of entering isobutylene)	268	253	21.3	290	15.2	13.0	20.4

GASEOUS PRODUCTS FORMED PER LITER OF *Iso*BUTYLENE ENTERING

Propylene, cc.	127	105	133	129	146	158	129
Methane, cc.	420	372	426	534	238	507	310
Isobutane, cc.	20	92	53	36	15	34	23
Hydrogen, cc.	167	143	105	193	168	(−35)	131
Acetylene, cc.	9	11	10	7	4	6	14
Oxides of carbon, cc.	9	6	0	4	12	8	11
Ethylene and aromatics, cc.	79	27	38	66	84	105	58

GASEOUS PRODUCTS FORMED PER LITER OF ISOBUTYLENE DECOMPOSED

Propylene, cc.	202	195	259	201	268	278	249
Methane, cc.	669	689	830	830	438	894	600
Isobutane, cc.	32	169?	103?	56	28	60	44
Hydrogen, cc.	266	265	204	300	309	(−62)	253
Acetylene, cc.	14	20	20	11	7	11	27
Ethylene and aromatics, cc.	126	50	74	103	155	185	112

OIL FORMATION

Yield of oil, based on the weight of *iso*butylene decomposed, %	42 7	46 8	41 5	45	28.0	22 9	39.4

tion. A volume of **21.3** liters **(53.4** g.) of isobutylene (0°, 760 mm.) was passed through the reaction tube. The volume increase was 20.9%.

After removing the excess bromine from the solution of the bromides, the carbon tetrachloride was distilled off. Of the residue, the lower-boiling portion (b. p. **(30** mm.) 51–68"), which contained the ethylene, propylene and isobutylene dibromides, was found to weigh **94.3** g. The higher-boiling material weighed **43.2** g. After four fractionations with a fractionating column of the type described by Cooper and Fasce,[8] the dibromides were separated into the following fractions

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[8] Cooper and Fasce, *Ind. Eng. Chem.*, 20,420 (1928).

B. p., °C.	130–139	138–144	145–148
Grams	4.4	21.1	55.2
n_D^{20}	1.5178	1.5158	1.5111

and the residue was added to the first high-boiling residue. The amounts of ethylene bromide, propylene and *iso*butylene bromide were estimated from the distillation curve and also from the refractive index[4] of the three fractions.

Dibromides	Ethylene	Propylene	*Iso*butylene
From refr. index, g.	..	18	63
From distn. curves, g.	1	18	62

The higher-boiling material from the bromides was fractionated at reduced pressure and was also shown to represent isobutylene for the most part. The largest fraction was tribromo-isobutane, which is formed along with higher brominated products when isobutylene reacts with bromine? Considerable tetrabromo-isobutane was found, and also a small residue containing presumably penta- and hexa-substituted *iso*butane. There was also a very small fraction containing acetylene tetrabromide and possibly allene tetrabromide. No butadiene tetrabromide was found, contrary to the work of A. A. Noyes.[5]

Most of the tribromo-isobutane was collected at 75.2–76° (4 mm.); its index of refraction was n_D^{20} **1.5670.** Between **81** and 88°, **4.5** g. of similar material was also collected. Only half a gram distilled in the next fraction at **108–110"** (9 mm.), n_D^{20} **1.5728.** This fraction should represent the acetylene or allene tetrabromides. The next fraction of tetrabromo-*iso*butane weighed **5.8** g. It was collected at **134–150" (15** mm.), and its index of refraction at 20° was **1.6070.** The residue weighed **1.8** g.

On the basis of **123** g. of isolated bromides, 1 g. was from ethylene, **18** g. from propylene, 95 g. from isobutylene (as di-, tri-, or polybromides) and 9 g. of other bromides. The mole percentage of olefins by such an analysis is ethylene **1.0%;** propylene 17.2%, isobutylene 76.0%, others **5.8%.** These results agree closely with the results by absorption methods in the modified Orsat apparatus.

	By absorption. %	Calcd. from bromides, %
Isobutylene	40.6	40.7 (53.6 X 0.760)
Propylene	8.4	9.2 (53.6 X 0.172)
Ethylene	2.4	0.5 (53.6 X 0.010)
Acetylene	2.2	3.2 (remainder)
	53.6	53.6

Reaction of Bromine and Isobutylene.—The proportion of the different bromination products given when *iso*butylene reacts with bromine has been calculated from the results of this fractionation. It is interesting to com-

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[9] Mereshkowsky, Ann., 431, 113 (1923).

pare our results at 0–5° with those of Mereshkowsky[9] at 45–50°. Evidently the bromination of isobutylene dibromide is lessened at the lower temperature, but it is still remarkably large as compared with similar experiments on other olefins which are reported in the literature.

	This investigation, 0–5°		Mereshkowsky, 45–50°	
*Iso*butylene dibromide	65.5	% by weight	45	% by weight
Tribromo-*iso*butane	25.5		44	
Tetrabromo-*iso*butanes	6.0		7	
Penta- and hexa-analogs	3.0		1	

The Liquid Products.—The pyrolysis of isobutylene is complicated by the formation of large amounts of liquid products in addition to the gaseous products which have been discussed. When the isobutylene was diluted with nitrogen before passing into the hot tube, the yield of liquid products was appreciably decreased (see Table VA, Expt. 12). Dilution with hydrogen had a similar effect on the yield of liquid products and in addition it served to increase the yield of methane and of propylene appreciably. Also it seemed to increase the yield of gaseous saturated hydrocarbons other than methane (see Table VA, Expt. 13). The accuracy of the combustion method for the determination of such saturated hydrocarbons is open to some question since all of the benzene and toluene vapors may not have been removed by the fuming sulfuric acid (8% free SO_3) before the combustion. The use of stronger acid, on the other hand, would result in the solution of appreciable quantities of such hydrocarbons as *iso*butane and propane.[10] The experiment with hydrogen is rather good evidence that the following reactions of scission and addition normally occur to some extent with the hydrogen which is liberated in the reaction.

$$(CH_3)_2C{=}CH_2 + H_2 \longrightarrow CH_4 + CH_3CH{=}CH_2$$
$$(CH_3)_2C{=}CH_2 + 2H_2 \longrightarrow 2CH_4 + CH_2{=}CH_2$$
$$(CH_3)_2C{=}CH_2 + H_2 \longrightarrow (CH_3)_3CH$$

The important part played in the reaction by the formation of the liquid products is shown in Table VI, in which the yield of liquid products is given in percentage by weight of the isobutylene decomposed.

TABLE VI

LIQUID PRODUCTS FROM *ISO*BUTYLENE

Temp., °C.	Contact time, sec.	Yield, %	Temp., °C.	Contact time, sec.	Yield, %
650	13	63	700	19	49
650	27	40	700	22	43
			700	23	47
700	12	47	700	25	42
700	18	63	700	32	45

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[10] Worstall, Am. Chem. J., 20, 664 (1898); THIS JOURNAL, 21, 246 (1899); Orndorff and Young, Am. Chem. J., 15, 261 (1893).

Examination of the Oils Formed at 700°.—The density of the oil formed from isobutylene at 700° was found to increase with the contact time. This would be expected, since, as the contact time increases, the reaction of the aromatic hydrocarbons with each other and with the unsaturated hydrocarbons present forms the higher molecular weight aromatic hydrocarbons. The density, for a contact time of twelve seconds, was d_4^{20} 0.8511; for twenty-four seconds, d_4^{20} 0.8899; and for thirty-two seconds, d_4^{20} 0.9053.

Two samples of the liquids were fractionated, with the following results.

B. p., °C.	Weight, g.	% by weight of the oils	B. p., °C.	Weight, g.	% by weight of the oils
65–96	6.2	20.0	65–103	6.8	20.5
97–122	8.5	28.0	103–105	7.0	21.0
137–146	3.5	11.5	125–155	3.0	9.0
146–180	3.8	12.5	170–205	2.2	6.7
180–275	1.5	5.0	205–218	2.2	6.7
275–310	1.0	3.5	230–330	2.2	6.7
310–330	1.0	3.5	360–395	0.3	0.9
Pitch	2.5	8.0	Residue	3.5	10.5
Loss	2.4	8.0	Loss	5.9	18.0
	30.4	100.0		33.1	100.0

The fractions of similar boiling point were then combined and fractionated more closely to separate the individual hydrocarbons. Much of the distillation loss in these fractionations was due to the dissolved *iso*butylene,[11] the last traces of which are removed with difficulty by distillation processes. Table VII shows the results of the final fractionation.

TABLE VII

FINAL FRACTIONATION OF OILS FROM *ISO*BUTYLENE

Fraction	Boiling range. °C.	Weight, g.	n_D^{20}	Probable composition
A	Up to 76°	1.2	....	Benzene and isobutylene
B	77–85	5.1	1.4850	Benzene and isobutylene
C	89–109	5.9	1.4860	Benzene and toluene
D	109–113	9.9	1.4912	Toluene
E	118–133	2.5	....	......
F	135–143	4.6	1.5005	Xylenes
G	153–185	3.5	1.5258	......
H	190–250	5.4	Naphthalene and homologs	
I	250–300	3.3	Diphenyl, ditolyl (?)	
J	310–395	1.3	Anthracene, phenanthrene	

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[11] Brooks, "The Non-Benzenoid Hydrocarbons," The Chemical Catalog Co., Inc., New York, 1923, p. 583: "Kerosene and machine oil dissolve about 220 volumes of isobutylene at room temperature and the gas is only completely expelled on heating to 260°." Benzene–toluene mixtures would probably act similarly, since their solvent action is usually greater.

From the results in Table VII, only Fraction A gave evidence of the presence of appreciable amounts of unsaturated hydrocarbons by the usual tests. The high refractive indices of the fractions are also indicative of the aromatic nature of the hydrocarbons. The following derivatives were prepared.

Fraction	Derivative	Obs. m. p., °C.	Recorded lit. m. p., °C.	Mixed m. p., °C.
B	*m*-Dinitrobenzene	89.5–90	90	90–90.5
D	Trinitrotoluene	80–81	82	81–82
F	Nitro derivative	127–129	178, trinitro-o-xylene 182, trinitro-*m*-xylene 139, trinitro-p-xylene	
H	Picrate	128–131		
		125–134	150, naphthalene picrate	
J	Picrate	142–145	143, phenanthrene picrate	
		157–164	161, anthracene picrate	

Benzene and toluene were thus definitely characterized by their derivatives. The other fractions undoubtedly contained several compounds, since the derivatives were impure after two recrystallizations.

Isobutylene and Isobutane Compared.—Under comparable conditions isobutylene differs quite materially from isobutane in its behavior toward heat, in spite of the fact that both of these substances are branched hydrocarbons which contain four carbon atoms. For example, at 600° the unsaturated hydrocarbon decomposed only 1.2% in eighteen seconds, whereas the saturated hydrocarbon decomposed 13–19.5% in seventeen to twenty-one seconds.[4] For a 20% decomposition of isobutylene at 600°, a hot contact period of 200 seconds was required. With 700° temperatures, the rate of decomposition for both hydrocarbons is markedly increased although the contrast is still apparent. For a hot contact time of twelve to twenty-one seconds, isobutane was broken down to the extent of 70%, whereas with isobutylene decomposition varied between 30 and 50%.

Still more striking a difference in the two cases is to be found in the course of the two reactions. Isobutane was found to decompose almost exclusively into gaseous hydrocarbons which were molecularly smaller than the original substance. Isobutylene, on the contrary, changed quite materially into hydrocarbons of greater molecular complexity. Nearly half of the decomposed isobutylene gave rise to liquid hydrocarbons whereas the remainder appeared in the form of gases. The gaseous products from both isobutane and isobutylene were similar to the extent that methane, hydrogen and propylene were important products of the decomposition, with methane always predominating.

The Mechanism of the Pyrolysis.—Any mechanism for the pyrolysis of isobutylene must provide an explanation not only for the simpler gaseous hydrocarbons of the reaction but also for the generous formation of aromatic hydrocarbons. As major effects, it is suggested that heat may rupture the single C—C or C—H bonds, and that it may activate the C=C double bond. The univalent radicals which are thought to be formed by rupture of the single bonds, namely, $-CH_2-C(CH_3)=CH_2$ or $-C(CH_3)=CH_2$, evidently do not give rise as such to aromatics, since the quantity of liquids formed during pyrolysis of the butanes was very small and since, for the butanes, transient radical formation was also postulated. Such univalent radicals appear to give rise to gaseous products. In the case of the double bond, it is considered that the tie is sufficiently strong to resist complete rupture, thereby creating a radical with two bonds. In the case of *iso*butylene, this is $(CH_3)_2\underset{|}{C}-\underset{|}{C}H_2$. As a working hypothesis it is considered that radicals of the latter type are the precursors of building-up processes. Three such "activated olefin molecules," by combination, would produce a cyclohexane derivative which, at the elevated temperature of formation, would be stripped into benzene derivatives,

Summary

Isobutylene was found to be a more stable hydrocarbon than *iso*butane or n-butane. It was only slowly decomposed at 600°. The pyrolytic reactions were studied at 600, 650 and 700°, especially at 700° where the rate of decomposition was rather high. It was demonstrated that the reaction was unimolecular and largely homogeneous. The velocity constant and the heat of activation for the unimolecular reaction were calculated from the data. The various products of the reaction were identified. The mechanism of the reaction is much more complicated than that of the saturated hydrocarbons studied, but a mechanism is suggested which recognizes not only the decomposition into smaller substances but also the building-up processes into aromatic hydrocarbons.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHTS OF PHYCOCYAN AND OF PHYCOERYTHRIN FROM PORPHYRA TENERA AND OF PHYCOCYAN FROM APHANIZOMENON FLOS AQUAE

BY THE SVEDBERG AND TOMINOSUKE KATSURAI

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In a previous paper a report has been given of the determination of the molecular weights of phycocyan and phycoerythrin from *Ceramium rubrum* by means of the centrifugal methods developed in this Laboratory.[1] For phycocyan the value 106,000 ± 5000 was found within the PH region 6.8–7.9 and for phycoerythrin the value 208,000 ± 8000 within the PH region 5.0–6.8. It was pointed out that within the limits of experimental error these values are equal to the molecular weight of egg albumin, 34,500, multiplied by the integers *three* and *six*, respectively. It seemed desirable to extend this study to proteins from other algae and to make determinations within *a* wider *PH* range in order to state the stability regions of these proteins. The alga *Porphyra tenera* was chosen as a representative of the *Rhodophyceae* group not too closely related to *Ceramium*. As a representative of the *Cyanophyceae*, the blue-green algae, *Aphanizomenon flos aquae* was chosen.

Experimental

Preparation of Material

Preparation of Phycocyan and Phycoerythrin from Porphyra tenera.—The Japanese product, "Nori," which consists of dried *Porphyra tenera* was extracted with water as described by Kitasato;[2] 2800 g. was used for this work. Four hundred cc. of water was added for each 10 g. of the material, which was kept in the dark. After some days 1% of toluene was added as a preservative and the extraction was carried on for three weeks. In this way a reddish-violet colored solution was obtained. This solution was treated with about 20% of its weight of ammonium sulfate. The proteins thus precipitated were separated by centrifuging in a bucket centrifuge and brought into solution by washing with distilled water. This solution was then treated with increasing amounts of ammonium sulfate up to 25% of its weight. After each addition it was allowed to stand for a day. The precipitate formed was separated by centrifuging. In this way several mixtures containing different relative amounts of the two substances were formed.

The mixed precipitate was washed with cold water, under which conditions the phycocyan dissolved much quicker than phycoerythrin. By repeating the precipitation with ammonium sulfate and washing the precipitate with cold water, the separation of these substances was carried out completely.

Preparation of Phycocyan from Aphanizomenon flos aquae.[3]—The weed was collected from the surface of a lake near Upsala. The fresh material (30 kg.) was freed

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[1] Svedberg and Lewis, THIS JOURNAL, **50**, 525 (1928).

[2] Kitasato, "Acta Phytochimica," 2, 75 (1925).

[3] The preparation of this protein was carried out by Mr. Arne Tiselius.

from excess of water on a cloth filter and the residue was left to stand for three days, allowing autolysis to set in. Some gas was evolved and the phycocyan began to penetrate the cell membranes.

At this time the putrefaction was stopped by the addition of toluene. After five days the material was centrifuged and the residue was discarded. The supernatant liquid has a blue-green color and is fluorescent. To this a saturated ammonium sulfate solution was added in the proportion of 700 cc. of the ammonium sulfate to 1000 cc. of the liquid. The precipitate thus formed was separated by centrifuging and dissolved in distilled water. Recrystallization was repeated three times with the addition of one volume of saturated ammonium sulfate to five volumes of the solution. The first mother liquor formed by the addition of ammonium sulfate was green. As the process of recrystallization proceeded it became deep blue and strongly fluorescent. Well-defined crystals were formed when the precipitate was kept in an ice box for some days. A photomicrograph of the crystals is shown in Fig. 1. The crystals were dissolved in water and dialyzed against phosphate buffer (PH 6.8) and against acetate buffer (PH 4.6). The mother liquor was also dialyzed in the same way.

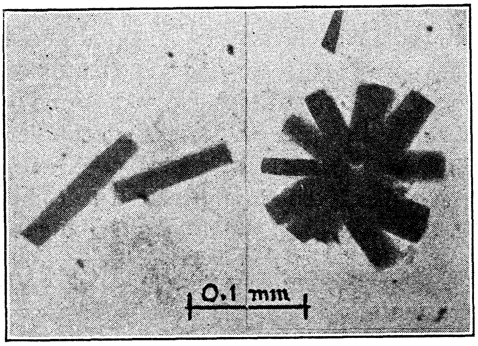

Fig. 1.

Specific Volume.—The partial specific volume was determined pycnometrically at 19.8". The amount of protein in solution was determined by drying a certain amount of the solution at 105" and subtracting the amount of salt in the sample as known from the composition of the buffer.

The value 0.759 was obtained for phycocyan from *Porphyra tenera* at PH 6.8 (solvent 0.0167 M in KH_2PO_4 and in Na_2HPO_4). The determination by A. Tiselius in this Laboratory gave 0.755 for phycocyan from *Ceramium rubrum*. The average value 0.746 was obtained for phycocyan from *Aphanizomenon flos aquae* at various hydrogen-ion concentrations between PH 4.6 and 12.0 (solvent: for PH 4.6, 0.01 M in acetic acid and in sodium acetate; for *PH* 12.0, 0.01 M in Na_2HPO_4 and 0.00864 M in NaOH). No appreciable change with PH was observed. The average value was further found to be almost identical with the values obtained by previous determinations for egg albumin,' hemoglobin: serum albumin and serum globulin: phycocyan and phycoerythrin (from *Ceramium rubrum*).[1]

Light Absorption.—The absorption in the visible spectrum was measured with a Konig–Martens spectrophotometer, and in the ultraviolet with a Judd–Lewis spectrophotometer. Phycocyan and phycoerythrin from *Porphyra tenera* and *Ceramium rubrum* were studied at PH 6.8. The ultraviolet absorption of the phycocyan from *Aphanizomenon flos aquae* was measured at different hydrogen-ion concentrations. No change was observed between PH 4.6 to 6.8, but an appreciable change took place

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[4] Svedberg and Nichols, THIS JOURNAL, 48, 3081 (1926).

[5] Svedberg and Fåhraeus, *ibid.*, 48, 430 (1926); Svedberg and Nichols, *ibid.*, 49, 2920 (1927).

[6] Svedberg and Sjögren, *ibid.*, 50, 3321 (1928).

at *P*H 12.0, where the protein begins to decompose. The chief results are given in Figs. 2, 3 and 4. The specific extinction coefficient, $\epsilon/c = 1/cd \log (I_0/I)$ (where c is the concentration in per cent., d the thickness of the solution, I_0 the intensity of the light after passing through the solvent and I the intensity after passing through the same thickness of solution) is plotted against the wave length. Figure 2, which contains the curves for phycoerythrin from *Ceramium* (solid line) and from *Porphyra* (dotted

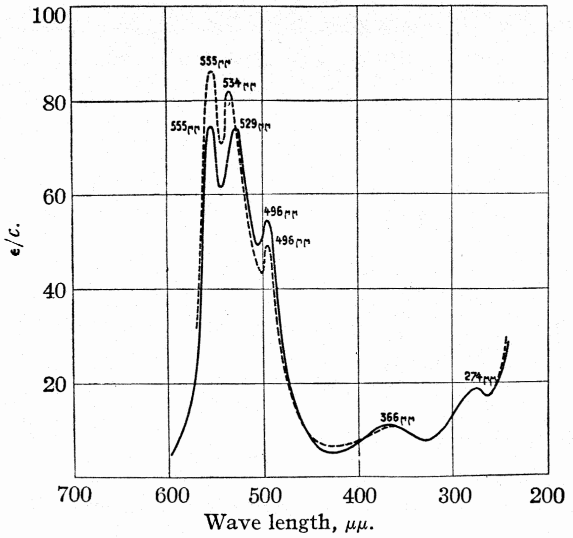

Fig. 2.

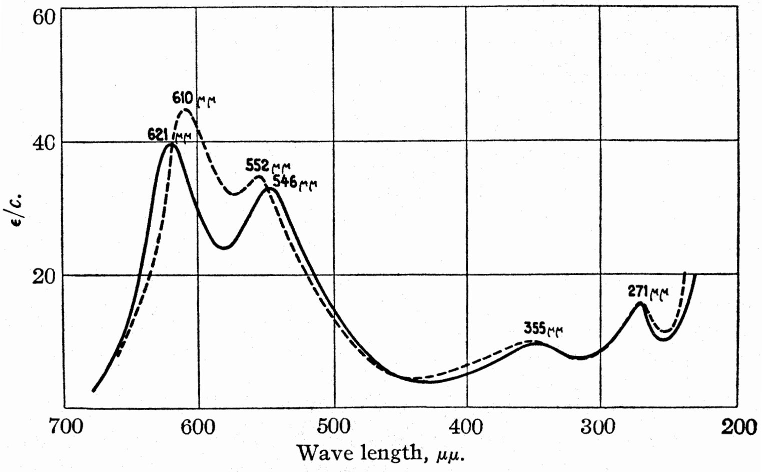

Fig. 3.

line), shows clearly the resemblance of the light absorption of these proteins, as does Fig. **3** in the case of phycocyan from the same two algae. Figure 4 shows that the visible absorption of phycocyan from *Aphanizomenon* is quite different from the absorption of phycocyan from *Ceramium* and *Porphyra*. In the ultraviolet, however, the absorption of phycocyan from *Aphanizomenon* is almost identical with that of phycocyan from *Ceramium* and *Porphyra*. For the purpose of comparing the results obtained with the values obtained previously by different authors, the positions of the maxima are shown in Table I.

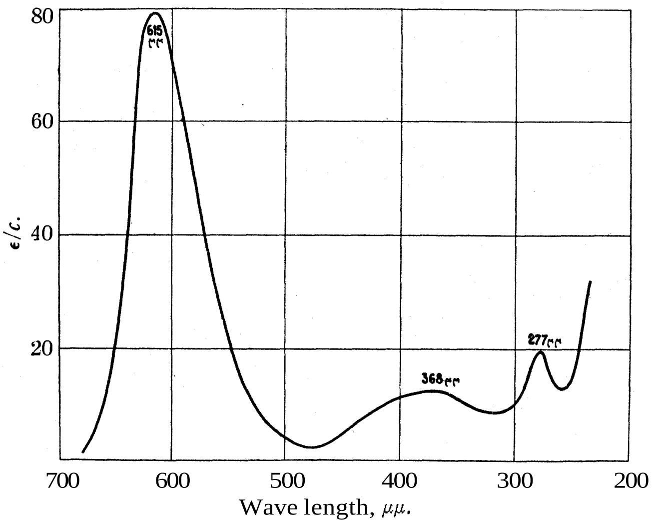

Fig. 4.

TABLE I

POSITION OF LIGHT ABSORPTION MAXIMA

	Phycocyan from *Ceramium rubrum*		Phycocyan from *Porphyra tenera*	
Prepared by	Kylin[7]	Tiselius	Kitasato	Katsurai
Observed by	Kylin	Katsurai	Kitasato[2]	Katsurai
Orange band	618–613	621	614	610
Yellow band	553–549	546	546	552
Long wave ultraviolet band	.....	*350*	330	355
Short wave ultraviolet band	.....	271	270	271

The values of the extinction coefficients obtained by Lewis in the ultraviolet region were found to be in error, probably owing to some toluene present. To secure freedom from toluene a current of wet nitrogen gas was blown through the protein solution just before the measurements were made.

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[7] Kylin, Z. *physiol. Chem.*, 69, 169 (1910).

TABLE II

POSITION OF LIGHT ABSORPTION MAXIMA

	Phycoerythrin from *Ceramium rubrum*					Phycoerythrin from *Porphyra tenera*	
Prepared by	Lewis	Lewis	Kylin	Kylin	Tiselius	Kitasato	Katsurai
Observed by	Lewis	Katsurai	Kylin	Katsurai[8]	Katsurai	Kitasato	Katsurai
Yellow band	566	554	569–565	554	560	662	555
Green band	540	528	541–537	536	533	526	534
Blue - green band	497.5	496	498492	498	496	495	496
Long wave uv. band	360	368	....	366	366	330	366
Short wave uv. band	262	275	...	275	275	270	272

TABLE III

POSITION OF LIGHT ABSORPTION MAXIMA

	Phycocyan from *Aphanizomenon flos aquae*	
Prepared by	Tiselius	Boresch[9]
Observed by	Katsurai	Boresch
Orange band	615	620
Long wave ultraviolet band	368	...
Short wave ultraviolet band	277	...

Determination of the Molecular Weight

The molecular weights were determined by the sedimentation velocity and the sedimentation equilibrium methods. The apparatus and procedure have already been described.[10,4,5] The photographs were taken by using the mercury line $\lambda = 366\mu\mu$. In order to cut off the other lines, Wratten nickel-glass was used as a light filter. In the case of the sedimentation velocity method the molecular weight is given by the relation

$$M = \frac{RTs}{(1 - V\rho)\,D}$$

where R is the gas constant, T the absolute temperature, s the sedimentation constant[11] or $1/\omega^2 x \cdot dx/dt$, D the diffusion constant, V the partial specific volume of the protein, ρ the density of the solvent, x the distance from the axis of rotation, ω the angular velocity and t the time. The values of the specific sedimentation velocity and of the diffusion constant were all reduced to 20° by means of the relations $s_1/s_2 = \eta_2/\eta_1$ and $D_1/D_2 = T_1/T_2 \cdot \eta_2/\eta_1$, where η is the viscosity of the solution.

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[8] The light absorption of phycoerythrin seventeen years old was measured; ref. 1, p. 532.

[9] Boresch, Biochem. *Z.*, 119, 167 (1921).

[10] Svedberg, *Z. physik. Chem.*, 121, 65 (1926); 127, 51 (1927).

[11] The term "Sedimentation Constant" has been adopted as a simplified means of expressing the old term "Specific Sedimentation Velocity."

In the case of the sedimentation equilibrium method, the molecular weight is given by

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)}$$

where R, T, V, ρ and ω have their usual meaning and c_1 and c_2 are the concentrations at the distances x_1 and x_2 from the center of rotation. In all, 51 runs were carried out. The results of all of the determinations are given.

Phycocyan from Porphyra tenera.—The values obtained for the sedimentation constant were independent of the time of centrifuging, but the diffusion constant showed a drift with the time, thus indicating slight heterogeneity of the material. The presence of a non-centrifugible substance was also observed. The value of the diffusion constant used for calculating the molecular weight was computed by an extrapolation procedure, as in the case of edestin.[12] The results of each of the runs are given in Table IV. For PH 4.6 and 6.8 the same buffers were used as previously mentioned; for *PH* 11.0 the buffer was 0.0172 M in Na_2HPO_4 and 0.00282 M in NaOH.

TABLE IV

SEDIMENTATION VELOCITY MEASUREMENTS ON PHYCOCYAN FROM *Porphyra tenera*

Concn., %	PH	R.p.m., mean	s, cm./sec. × 10^{13}	D × 10^7, cm.^{2}/sec.	*M*	Concn. of non-centrifugible matter, %
0.17	4.6	24,000	11.11	4.80	206.000	0
.37	6.8	43,000	5.69	5.30	109.000	10
.12	6.8	24,000	6.27	6.10	105.000	35
.10	11.0	41,000	2.06			10

As may be seen from the above table, the protein consists chiefly of molecules of the molecular weight of about 107,000 at *PH* 6.8. It is extremely interesting that the molecular weight is about doubled at *PH* 4.6 near the isoelectric point. At a *PH* of 9.7 the molecules seem to be breaking up, as the *s* is slightly lower than at *PH* 6.8. At higher *PH* (11.0) the protein breaks up into small molecules of various sizes.

Determinations of the molecular weight by the sedimentation equilibrium method were carried out at *PH* 6.8.

Values from 32,000 to 104,000 were obtained in one of the runs, and values ranging from 42,000 to 124,000 in the other. These results show that the molecules are not uniform. This protein contains to some extent molecules of a molecular weight smaller than 107,000.

In the case of Lewis's measurement of the molecular weight of phycocyan from *Ceramium rubrum*, the protein was prepared from the wet algae which was not dried by the sunlight, and the results of the determination of molecular weight have shown that the molecules are quite uniform. In

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[12] Svedberg and Stamm, THIS JOURNAL, 51,2170 (1929).

the present work the protein was prepared from the sun-dried material, and the results of the determination show that the molecules are not uniform and that the material contains some smaller molecule.

In order to see the effect of sun drying, the protein was prepared from sun-dried *Ceramium rubrum* and the molecular weight was determined at the same PH. As the yield of the protein was very small, only one run could be made but the result showed that part of the molecules were decomposed into smaller ones. The chief part of the phycocyan apparently had been completely destroyed in the drying process. This seems to explain the fact that the phycocyan used in the above experiments which had been prepared from sun-dried material did contain to some extent molecules of various sizes.

Phycoerythrin from Porphyra tenera.—In this case both the sedimentation and the diffusion constants were independent of time of centrifuging, thus indicating that the molecules had a uniform mass. Details of a typical run are given in Table V, and the results of all the runs are summarized in Table VI.

TABLE V

TYPICAL SEDIMENTATION VELOCITY RUN WITH PHYCOERYTHRIN FROM *Porphyra tenera*

Concentration, 0.12%; phosphate buffer ($M/60$ in KH_2PO_4 and in Na_2HPO_4) PH, 6.8; V, 0.747 at 19.8; ρ, 1000; T, 293; length of column, 1.22 cm ; thickness of column, 0.60 cm.; exposure, 30 sec.; mean speed 22,630 r.p.m. ($\omega = 2370$).

Time interval, min.	Δx per 30 min., cm.	Mean x, cm.	$\omega^2 x \times 10^{-7}$	s, cm /sec. $\times 10^{13}$	D, cm ^{2}/sec. $\times 10^7$
45– 75	0.060	4.950	2.77	12.14	6.06
75–105	.070	5.020	2.82	13.84	6.25
105–135	.065	5.085	2.85	12.33	6.12
135–165	.065	5.150	2.88	12.28	6.60
165–195	.065	5.215	2.92	11.83	5.54
195–225	.065	5.280	2.96	11 11	5.13
			Mean	12.25×10^{-13}	5.95×10^{-7}

Molecular weight, 199,000.

TABLE VI

SEDIMENTATION VELOCITY MEASUREMENTS ON PHYCOERYTHRIN FROM *Porphyra tenera*

Concn., %	PH	Mean speed, r.p.m.	s, cm /sec. $\times 10^{13}$	D, cm.^{2}/sec. $\times 10^7$
0.17	4.6	24,000	11.90	5.00
.65	6.8	43,000	10 90	5.00
.32	6.8	43,000	11 82	5.48
.16	6.8	43,000	11.11	4.55
.16	6.8	22,000	11.71	5 94
.12	6.8	22,630	12.25	5.95
.08	6.8	23,000	11 86	4.77
		Mean	11.65×10^{-13}	5.27×10^{-7}

Mean molecular weight, 214,000.

The values of the sedimentation constant and of the diffusion constant found by Lewis for phycoerythrin from *Ceramium* were 11.30 × 10^{-13} and 5.22 X 10^{-7}, respectively.

The results of the determination of the molecular weight by the sedimentation equilibrium method (using a wave length of 366$\mu\mu$ for illumination) showed that the molecules are of uniform size with a molecular weight of 213,000. The run made with a shorter wave length ($\lambda = 270\mu\mu$) showed that the molecules are not uniform, indicating that the protein has decomposed and that the decomposition products contain no chromophore group.

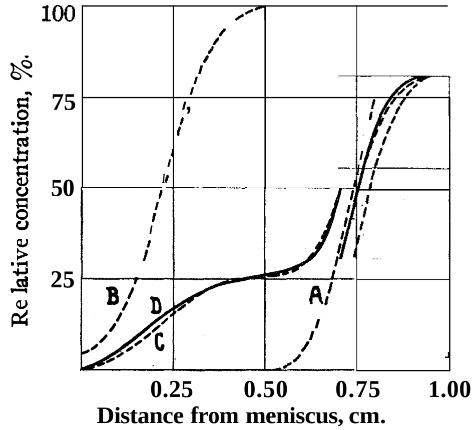

Fig. 5.

A run was made at **PH** 11.0 (phosphate buffer 0.0172 M in Na_2HPO_4 and 0.0028 *M* in NaOH). The speed was 42,000 r.p.m. and the temperature in the cell was 21.4°. In this case there was a large drift in the diffusion constant with time. From the diffusion curve it was calculated that the protein consisted of 75% of molecular weight 208,000 and 25% of molecular weight 34,600 ($^1/_6$ X 208,000). Figure 5 shows the calculated (C) and the experimental (D) relation between concentration and distance from meniscus after two hours of centrifuging, as well as the curves calculated for the cases in which the solutions were composed only of molecules of mass 208,000 (A) or only of molecules of mass $^1/_6$ × 208,000 (B).

Phycocyan from Aphanizomenon flos aquae.—Throughout the low-speed runs (mean r.p.m. 24,000) the values obtained for the sedimentation constant were independent of the time of centrifuging, but a drift of the diffusion constant was observed, showing the heterogeneity of the molecules. Formation of a non-centrifugible substance was observed. From the diffusion curves of the runs made at high speed (r.p.m. 44,000) the proportion of the molecules of the different molecular weight was calculated. The results of the determination of the sedimentation constant in a low-speed run are summarized in Table VII.

The high-speed run (r.p.m. 44,000) at the same **PH** showed that the protein molecules consist of 65% of molecular weight 208,000 and 35% of 104,000. For the purpose of seeing whether any separation can be effected by recrystallization, 10% of ammonium sulfate was added to the solution and the supernatant liquid was dialyzed against the same phos-

TABLE VII

SEDIMENTATION VELOCITY MEASUREMENTS ON PHYCOCYAN FROM *Aphanizomenon flos aquae* AT *PH* 6.8

Concn., %	Mean speed, r.p.m.	s, cm./sec. $\times 10^{13}$	Non-centrifugible subs., %
0.11	24,000	11.66	6
.11	24,000	11.41	0
.11	23,000	10.87	3
.12	24,000	11.75	1
.24	23,000	10.82	0
.40	24,000	11.98	0
	Mean	11.41×10^{-13}	

phate buffer solution. The solution thus obtained was studied with a high-speed run. As the result of experiment, 63% of 208,000 and 37% of 104,000 was obtained, showing that practically no separation takes place by fractional crystallization. It is quite interesting to notice that a run carried out at *PH* 4.6 showed that the protein molecules in this region are uniform, and have a molecular weight of 223,000. Figure 6 gives the calculated (C) and the experimental (D) relations between the concentration and distance from meniscus after 105 minutes for a solution of PH 6.8, at 44,000 r.p.m. and 20°. The curves A and B represent the distribution of concentration in solutions containing only molecules of mass 208,000 and $^1/_2 \times 208{,}000$, respectively. From the experimental curve the sedimentation constant of the heavier component was found to be 11.15×10^{-13} and for the other component 5.77×10^{-13}. These values check very well with those found by Lewis for phycoerythrin and phycocyan from *Ceramium* at *PH* of 6.8 (reduced to 20°), which are 11.30×10^{-13} and 5.59×10^{-13}, respectively. From a run carried out at very low hydrogen-ion concentration (PH 12.0) the value 3.24×10^{-13} cm./sec. was obtained for the sedimentation constant, which is about the same as that of egg albumin, *viz.*, 3.32×10^{-13}, found by Nichols.

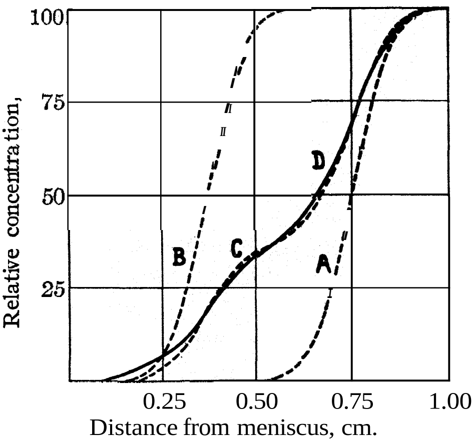

Fig. 6.

For the purpose of seeing whether the change of molecular weight by *PH* is reversible, a solution of *PH* 6.8 was dialyzed against acetate buffer of *PH* 4.6 and the solution thus obtained was studied. As the result of experiment the uniformity of molecules was observed and the value

252,000 was obtained for the molecular weight, showing that the change of molecular weight is reversible.

Determinations of the molecular weight by the sedimentation equilibrium method were also carried out. The protein solution used for the experiment was that obtained by dialyzing the dissolved protein crystals. Two runs made at P_H 6.8 showed that the molecules are of different molecular weight. In one run it was observed that the molecules have a molecular weight from 106,400 to 184,000 and from 117,000 to 200,000 in the other. The run carried out at P_H 4.6 showed the existence of molecules of molecular weight from 115,000 to 207,000.

Discussion of Results

From the results obtained in these experiments, it seems probable that the phycoerythrin from *Porphyra tenera* and from *Ceramium* are identical, and the same is true regarding phycocyan from those algae. The molecular weights and stability regions are probably identical, but further determination is necessary to decide this point completely. Tiselius' determination of the isoelectric points of phycoerythrin and phycocyan from *Ceramium rubrum* showed that these proteins have different isoelectric points, *viz.*, P_H 4.5 for phycocyan and P_H 4.3 for phycoerythrin.

The phycocyan from *Aphanizomenon flos aquae* is different from the above-mentioned proteins. It has a different light absorption and a different isoelectric point (P_H 4.7 as measured by Tiselius) and it seems that the stability region of the molecules is also different. If we consider 34,500 as the unit of the protein molecule and call it A, these proteins consist of molecules of molecular weight A, 3A and 6A, and mixtures of these molecules. It is worth noticing that the existence of the intermediate molecular weights 2A, 4A and 5A was not observed. More determinations are necessary to make up the complete chart of the molecular weights of these proteins as a function of P_H. For the sake of convenience, the names R-Phycoerythrin and R-Phycocyan are proposed for the proteins from *Porphyra tenera* and *Ceramium rubrum* from the name of the family *Rhodophyceae* to which they belong and C-Phycocyan for that from *Aphanizomenon flos aquae* from *Cyanophyceae*.

The expenses connected with these experiments have been defrayed by grants from the Nobel Fund of Chemistry and from the foundation "Therese och Johan Anderssons Minne."

Summary

1. The specific volume, light absorption and molecular weights of phycoerythrin and phycocyan from *Porphyra tenera* and of phycocyan from *Aphanizomenon flos aquae* have been determined at different hydrogen-ion concentrations.

2. The specific volumes of these proteins are identical and independent of PH and, within the limits of error, also identical with the specific volumes of all other proteins studied in this Laboratory, except the hemocyanins. This fact is in line with the result of the molecular weight determinations, according to which all the proteins in question are loosely built up of units of approximately the same mass, *viz.*, 34,500. It is also probable that they have the same general constitution.

3. The light absorption of the phycoerythrins from *Porphyra* and *Ceramium* are identical and the same is the case for the corresponding phycocyans. The light absorption of phycocyan from *Aphanizomenon* is different from that of the *Rhodophyceae* proteins.

4. Near the isoelectric points the molecular weights of these three proteins are identical and approximately 208,000 ± 5000. With increasing PH decomposition of the molecules takes place. The phycoerythrin is the most stable one. At PH 6.8 it is still undecomposed but at PH 11.0 it consists of a mixture of 75% 208,000 and 25% $^1/_6$ X 208,000. Phycocyan from *Porphyra* shows indications of decomposition at PH 6.8 but the bulk of it consists of $^1/_2$ X 208,000 at that PH; at PH 11.0 it is decomposed into small units of varying size. Phycocyan from *Aphanizomenon* is decomposed into a mixture of 65% of 208,000 and 35% of 100,000 at PH 6.8 and is completely decomposed into the protein unit $^1/_6$ X 208,000 at PH 12.0.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

THE PYROCHEMICAL DECOMPOSITION OF AZIBENZIL

BY JOHN J. RITTER AND GEORGE M. WIEDEMAN

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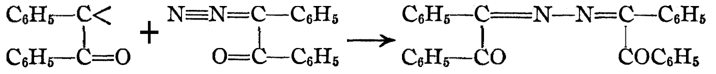
Introduction

Schroeter's[1] method for the preparation of diphenylketene has been recommended by Staudinger[2] in a slightly modified form as the most convenient source of that substance. The operations involved are (1) the preparation of benzil monohydrazone, (2) oxidation of this in benzene with mercuric oxide to azibenzil and (3) decomposition of azibenzil at 110–120° to nitrogen and diphenylketene in an atmosphere of carbon dioxide. During the preparation of diphenylketene in this Laboratory by this procedure certain hitherto unreported observations were made. The purpose of the present communication is to report on these, and also to describe a convenient and somewhat modified procedure used successfully by us in the synthesis of diphenylketene.

[1] Schroeter, *Ber.*, 42, 2336 (1909).

[2] Staudinger, *ibid.*, 44, 1619 (1911).

The decomposition of azibenzil into nitrogen and diphenylketene according to the procedure described by Staudinger yields, in addition, a viscous difficultly volatile nitrogen-containing residue. Staudinger[3] isolated from this residue a yellow crystalline solid melting at 201°, and assumed it to be a product of the addition of diphenylketene to azibenzil. We have noted that the residue yields, on distillation at ordinary pressure, benzonitrile and benzoic acid. The clue as to the source of these latter products was furnished by our further observation that *bis*-benzilketazine is also one of the products of the decomposition of azibenzil by heat. Its formation is apparently due to the addition of the desylene residue, formed by the loss of nitrogen from azibenzil, to a molecule of unchanged azibenzil



$$\begin{array}{l} C_6H_5-C< \\ \quad\;\; | \\ C_6H_5-C=O \end{array} + \begin{array}{l} N\equiv N=C-C_6H_5 \\ \qquad\quad\;\; | \\ \quad\;\; O=C-C_6H_5 \end{array} \longrightarrow \begin{array}{l} C_6H_5-C=\!=\!=N-N=C-C_6H_5 \\ \qquad\quad\;\, | \qquad\qquad\quad\;\; | \\ C_6H_5-CO \qquad\quad\;\; COC_6H_5 \end{array}$$

The formation of azines from aliphatic diazo compounds has been reported by Staudinger and Kupfer[4] and by Hellerman, Cohn and Hoen,[5] and has been explained by these investigators in an analogous manner. It seemed probable, furthermore, that the production of benzonitrile on distillation of the viscous residue from the heat decomposition of azibenzil was due to the presence of bis-benzilketazine. Meisenheimer and Heim[6] obtained, among other products, benzonitrile and stilbene on the distillation of benzaldazine; bis-benzilketazine would be expected to yield benzonitrile and dibenzoylstilbene, if it were to behave in a similar fashion. Curtius and Blumer,[7] who first prepared bis-benzilketazine, reported that it may be distilled without decomposition; Staudinger and Kupfer[4] state that it may be heated for two hours at 180–200° without alteration. We have observed that it yields, on distillation at ordinary pressure, benzonitrile and benzoic acid. It is therefore quite evident that the yellow solid isolated by Staudinger (m. p. 201°) is bis-benzilketazine (m. p. 202°, corr.).

Further study of the decomposition of azibenzil by heat showed that it may be converted to diphenylketene with a yield of 45% by suspending crystalline azibenzil in ligroin and refluxing the mixture for several hours.

Experimental Part

Benzil Monohydrazone.—The best method for the preparation of this compound was found to be the following modification of the procedure of Curtius and Thun:[8] 88 g. of benzil was dissolved in 220 cc. of boiling 95% alcohol in a 500-cc. three-necked flask fitted with a reflux condenser, mechanical stirrer and dropping funnel. The solution was stirred and refluxed while 50 g. of 42% hydrazine hydrate solution was

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[3] Staudinger, *Ber.*, **44**, 16 (1911).

[4] Staudinger and Kupfer, *ibid.*, 44, 2201 (1911).

[5] Hellerman, Cohn and Hoen, THIS JOURNAL, 50, 1716 (1928).

[6] Meisenheimer and Heim, *Ann.*, 355, 274 (1907).

[7] Curtius and Blumer, *J. prakt. Chem.*, [2] 52, 117, 137 (1895).

[8] Curtius and Thun, *ibid.*, [2] 44, 168 (1891).

slowly added during half an hour. After the hydrazine hydrate had been all added the mixture was refluxed for an additional two hours. During the heating a part of the sparingly soluble monohydrazone separated in crystalline form. After cooling of the mixture, **83** g. of crude monohydrazone was filtered off. The melting point of the crude product was 148–154°, corr. It was crystallized once from boiling 95% alcohol (0.06 g. per cc.), and the recrystallized product was found to melt at 151–152° (corr.). Curtius and Thun[8] report the melting point as 151°.

Oxidation of Benzil Monohydrazone.—Twenty-five grams of recrystallized finely divided benzil-monohydrazone was suspended in 200 cc. of ether in a 500-cc. flask and 25.5 g. of yellow mercuric oxide added. The mixture was stirred mechanically for four hours. The time required for complete oxidation was found to vary considerably with the character of the mercuric oxide used. Uniformly good results were obtained with mercuric oxide prepared in the following manner: 500 cc. of cold 0.3 *M* mercuric acetate solution was added to 200 cc. of cold 2.5 *M* sodium hydroxide solution. The mercuric oxide which was precipitated was washed repeatedly by decantation with cold water until free from alkali. It was then filtered with suction and air-dried. The most rapid oxidation of the hydrazone occurred when freshly prepared mercuric oxide was used; on standing for a short time in diffused daylight the latter decomposed partly with liberation of mercury, and in this condition was not suitable for use.

After completion of the oxidation the ethereal solution of azibenzil was filtered and dried over calcium chloride. It was then placed in a vacuum desiccator and the latter evacuated. After removal of the ether in this way, 17.7 g. of azibenzil, m. p. 79° corr., was obtained in good crystalline form. This method is substantially the same as that of Forster and Cardwell.[9]

Decomposition of Azibenzil by Heat. A.—Twenty-five grams of benzil monohydrazone was oxidized with mercuric oxide in dry benzene and the resulting solution of azibenzil dried over calcium chloride. This solution was then allowed to drop into a small distilling flask at 110–120° while nitrogen was passed continuously through the flask. These operations were carried out according to Staudinger's directions[2]

Diphenyl ketene was formed and removed from the reaction products by vacuum distillation in an atmosphere of nitrogen. A difficultly volatile viscous residue remained in the distilling flask. On distillation at ordinary pressure it yielded an oily distillate with the odor of benzonitrile, boiling from 167 to 189°. On cooling the distillate a portion of it solidified to a colorless crystalline mass.

B.—Seventeen and seven-tenths grams of crystalline azibenzil was suspended in 107 cc. of 60–90° ligroin which had been previously refluxed with potassium permanganate solution, washed and dried. The mixture was refluxed for eight hours on the water-bath, during which time the azibenzil slowly decomposed, the greater part of the decomposition products dissolving in the ligroin. After the azibenzil had disappeared, the solution was allowed to cool and was decanted from a small amount of bis-benzalketazine which was deposited on the walls of the flask during the reaction. The diphenyl ketene content of the ligroin solution was determined by precipitation with aniline and weighing of the diphenylacetanilide formed. Forty cc. of the solution gave 3.5 g. of diphenylacetanilide corresponding to a yield of 45% based on the azibenzil. The bis-benzilketazine melted at 202° (corr.) and its identity was established further by comparison with an authentic sample of the pure material, prepared as described in the following section.

Preparation of *Bis*-benzilketazine.—*Bis*-benzilketazine has been obtained by Curtius and Blumer[10] together with other products, by heating benzoin hydrazone alone

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[9] Forster and Cardwell, *J. Chem. Soc.*, 103,868 (1913).

[10] Curtius and Blumer, *J. prakt. Chem.*, [2] *52*, 132 (1895).

in alcoholic solution, or by passing hydrogen chloride into a suspension of benzoin hydrazone in ether. Curtius and Kastner[11] obtained it by dissolving benzil monohydrazone in sulfuric acid and pouring the solution into water at zero, or by heating benzil monohydrazone with benzil at 200'. Staudinger and Kupfer[4] heated benzil monohydrazone for two hours at 240° and also got bis-benzilketazine. We were unable to find any mention in the literature of the following simple method used in this work for its preparation.

Fifty grams of benzil was dissolved in 135 cc. of 95% alcohol, 14 g. of hydrazine hydrochloride dissolved in 30 cc. of boiling water was added and the solution boiled on the steam-bath for five minutes. The ketazine separates rapidly from the boiling solution as a voluminous yellow mass. It was filtered from the hot solution, washed with hot alcohol and recrystallized from boiling glacial acetic acid (0.25 g. per cc.). The yield is quantitative. The recrystallized product melted at 202° (corr.). Staudinger and Kupfer report 195–196°; Curtius and Blumer. 202". Our product, like that of Curtius and Blumer, yielded benzil on hydrolysis with aqueous sulfuric acid.

Distillation of *Bis*-benzilketazine.—Twelve grams of recrystallized material was placed in a distilling flask with a low side-arm, and distilled from a metal-bath through an air condenser. When the temperature of the bath reached 250°, a yellow oil began to distil over. Distillation was continued until the temperature of the bath reached 360". A thermometer placed in the vapor during the distillation read 167° at the beginning and 169° at the end of the distillation. A portion of the oily distillate solidified on cooling and was removed mechanically from the air condenser. The oil was found to boil at 189". This fraction was identified as benzonitrile by converting a portion of it to benzoic acid by hydrolysis. The solid which separated from the oil on cooling was identified as benzoic acid.

Summary

1. A modified procedure for the synthesis of diphenyl ketene by Schroeter's reaction has been described.
2. The decomposition of azibenzil by heat has been shown to yield *bis*-benzilketazine.
3. Distillation of bis-benzilketazine yields benzonitrile and benzoic acid.

NEW YORK, N. Y.

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[11] Curtius and Kastner, J. *prakt. Chem.*, 83, 215–232 (1911).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

SALTS OF TRIPHENYLSELENONIUM HYDROXIDE[1]

BY HENRY M. LEICESTER AND F. W. BERGSTROM

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In salts of the type of tetramethylammonium chloride, $(CH_3)_4NCl$, and trimethylsulfonium chloride, $(CH_3)_2SCl$, the radicals $(CH_3)_4N$ and $(CH_3)_3S$ play the part of metals, and like the metals can be arranged in an electropotential series or series of relative electro-affinities.[2] Tetramethylammonium and trimethylsulfonium thus occupy positions near the head of this series, comparable with the positions occupied by the alkali metals, which they resemble in character. Now it has customarily been assumed that replacement of one or more indifferent methyl groups by groups of a distinct negative character, such as phenyl, diminishes the electropositiveness of the radical as a whole. While this appears to be true in a qualitative sense[3] there are several apparent exceptions, notably the recently synthesized tri-, tetra- and pentaphenylchromium hydroxides,[4] which are bases of moderate strength in spite of the large number of negative phenyl groups in their molecules.

A determination of the effect of different alkyl or aryl groups upon the position of these substituted -onium radicals in the electropotential series would thus appear to be a problem worthy of further study. The present investigation was undertaken for the purpose of supplying such information for the little known trialkyl and triaryl selenonium groups. As a prelude to this work it was found necessary to devise an adequate method for the preparation of the selenonium salts. In this paper is reported the synthesis of some salts of triphenylselenonium hydroxide.

Jackson[5] prepared the first selenonium compound, trimethylselenonium iodide, $(CH_3)_3SeI$, as well as the corresponding dimethylbenzyl and the tribenzyl salts, the last named not being recognized until Fromm and Martin[6] proved its structure. Pieverling[7] made an extensive study of the triethylselenonium salts, and Pieroni and Coli[8] isolated the selenohydrate, $(C_2H_5)_3SeSeH$. Scott[9] prepared trimethyl- and triethylselenonium per-

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Presented at the Regional Meeting of the Pacific Division of the American Association for the Advancement of Science, at Berkeley, California, June, 1929.

[2] Kraus, THIS JOURNAL, 46, 2196 (1924); Kraus, "Radicals as Chemical Individuals," Columbia University Press, 1927.

[3] Hein and Meininger, Z. *anorg. allgem. Chem.*, 145, 95 (1925).

[4] Hein, *Ber.*, 54, 1905 (1921); Hein and Schwartzkopff, *ibid.*, 57, 8 (1924). The corresponding alkyl chromium hydroxides have not been prepared, and *so* are not available for comparison.

[5] Jackson, Ann., 179, 1 (1875).

[6] Fromm and Martin, *ibid.*, 401, 187 (1913).

[7] Pieverling, *ibid.*, 185, 331 (1877); *cf.* also Rathke, *ibid.*, 152, 210 (1869).

[8] Pieroni and Coli, *Gazz. chim. ital.*, II, 44, 349 (1914).

[9] Scott, *Proc. Chem. Soc.*, 20, 156 (1904).

iodides. This completes the work on the aliphatic salts. Hilditch and Smiles[10] prepared certain aromatic selenonium salts by the action of aluminum chloride upon anisole or phenetole and selenium dioxide. The yields were very low and the products impure. The structure of these compounds has recently been proved by Morgan and Burstall,[11] who have also prepared several hydroxyarylselenonium salts from phenols and selenium oxychloride. In addition, Carrara,[12] Pope and Neville,[13] and Edwards, Gaythwaite, Kenyon and Philips[14] have prepared compounds in which one of the three organic groups attached to the selenium atom is —CH_2COOH.

The selenium halides of the type $SeCl_4$ seem to offer an excellent starting point for the synthesis of compounds of the desired kind, due to the reactivity of the halogen atoms. However, it was found that too many side reactions occurred, and the Grignard, the Wurtz–Fittig, and the Friedel–Crafts reactions all yielded complex mixtures. It therefore seemed best to simplify the preparation by the use of a compound in which some of the halogen atoms of the selenium tetrahalide were already replaced by organic groups. Such a compound, diphenylselenium dichloride, $(C_6H_5)_2SeCl_2$, was successfully employed in a Friedel–Crafts reaction. The following equations represent the essential steps in the complete synthesis of triphenylselenonium chloride

$$\begin{aligned}
&2C_6H_5N_2Cl + K_2Se = (C_6H_5)_2Se + N_2 + 2KCl\\
&(C_6H_5)_2Se + O \overset{HNO_3}{=} (C_6H_5)_2SeO\\
&(C_6H_5)_2SeO + 2HCl = (C_6H_5)_2SeCl_2 + H_2O\\
&(C_6H_5)_2SeCl_2 + C_6H_6 \overset{AlCl_3}{=} (C_6H_5)_3SeCl + HCl
\end{aligned}$$

The chloride thus prepared forms a white, crystalline hydrate, $(C_6H_5)_3$-$SeCl\cdot 2H_2O$, with great ease on exposure to moist air. From the chloride it is easy to prepare other salts by double decomposition. Thus the water solution of the chloride yields a precipitate of the iodide or dichromate on treatment with a soluble salt of hydriodic or dichromic acid, an alcoholic solution of the chloride gives the picrate with picric acid, and the nitrate may be prepared by mixing aqueous solutions of the chloride with silver nitrate. In crystallizing the chloride from ethylene bromide, it was found that a quantitative conversion into triphenylselenonium bromide took place. This rather unusual reaction forms the best method for the preparation of the water-soluble bromide.

Another observation of some interest is that the melting points of the

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[10] Hilditch and Smiles, *J. Chem. Soc.*, *93*, 1384 (1908).

[11] Morgan and Burstall, *ibid.*, 3260 (1928).

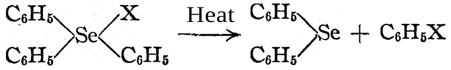
[12] Carrara, *Gazz. chim. ital.*, II, *24*, 173 (1894).

[13] Pope and Neville, *J. Chem. Soc.*, *81*, 1552 (1902).

[14] Edwards, Gaythwaite, Kenyon and Philips, *ibid.*, 2293 (1928).

chloride, bromide and iodide are very close to one another, 230, **236** and 237.5°, respectively. In a similar way the tri-(4-hydroxyphenyl)-selenonium chloride of Morgan and Burstall[11] melts at 232° and the bromide at 237°, while their tri-(3-methyl-4-hydroxyphenyl)-selenonium chloride melts at 231°. Since all these melting points are accompanied by decomposition, it appears that the breakdown at this temperature is rather a property of the selenonium type of molecule and is little affected by the substituent parts, as long as these are aryl in character.

In the case of the triphenylselenonium halides the decomposition occurs as follows



$$(C_6H_5)_2Se(X)(C_6H_5) \xrightarrow{\text{Heat}} (C_6H_5)_2Se + C_6H_5X$$

where X is a halogen atom. Presumably the other compounds mentioned decompose in an analogous fashion. This reaction is exactly similar to that of the trialkylselenonium halides, save that the latter is reversible. It was, in fact, this method which Pieverling[7] used in his synthesis, the reaction being

$$(C_2H_5)_2Se + C_2H_5I \longrightarrow (C_2H_5)_2SeI$$

At 80° the reverse reaction occurs and the two liquids on the left-hand side of the equation distil over, to reunite in the cold. The reaction in the aromatic series appears to be irreversible, however, and even ethyl iodide does not react with diphenyl selenide over a period of several months.

Experimental Part

Diphenyl Selenide.—This compound was at first prepared from diphenyl sulfone and selenium, according to the method of Krafft and Lyons.[15] However, an extension of the method of Schoeller[16] was found to be more rapid and economical. Three hundred and sixty grams of powdered potassium hydroxide and 240 g. of black, powdered selenium were thoroughly mixed and heated on an oil-bath to 140°, at which temperature they fused together. To a solution of the fused mass in 400 cc. of ice water was added slowly and in small portions at a time an ice cold solution of diazotized aniline hydrochloride from 138 g. aniline. To complete the reaction, the solution was separated from the viscous selenium-containing black mass in the bottom of the reaction vessel and heated to boiling. While still hot this was poured back upon the viscous black mass, which was then stirred up with the liquid.[17] The precipitate of selenium was filtered off and the lower liquid layer of the filtrate, consisting of diphenyl selenide, separated. The selenium was washed with ether or chloroform and the washings combined with the selenide. The combined liquids were distilled and the fraction boiling at 300–315° was the desired diphenyl selenide; yield, 125 g., or 72%, based upon the aniline used.

Diphenyl Selenium Dichloride.[18]—The diphenyl selenide (125 g.) was dissolved in an excess of commercial concentrated nitric acid and commercial concentrated hydrochloric acid was added. The dense yellow precipitate resulting was filtered, washed with

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[15] Krafft and Lyons, *Ber.,* 27, 1761 (1894).

[16] Schoeller, *ibid.,* 52, 1517 (1919).

[17] In this manner all danger of breaking the container was avoided.

[18] *Cf.* Zeise, *Ber.,* 28,1670 (1895); Foster and Brown, THIS JOURNAL, 50,1185 (1928).

water and crystallized once from benzene. The compound thus treated is still yellow, but is sufficiently pure to be used in the preparation of triphenylselenonium chloride; yield, 141 g., or 87%, calculated on the basis of the diphenyl selenide.

Triphenylselenonium Chloride, $(C_6H_5)_3SeCl$.—Eighty grams of anhydrous aluminum chloride was suspended in 100 cc. of dry benzene. The reaction flask was cooled with ice and 40 g. of diphenylseleniumdichloride was added in portions over a period of twenty minutes. The flask was cooled and shaken throughout the addition. If these precautions were not observed, the mixture became warm and the product was largely a tar. During the reaction the liquid became dark red-brown, the aluminum chloride dissolved and hydrochloric acid was given off. After all of the dichloride had been added the mixture was allowed to stand for three hours at room temperature; 200 cc. of water was then cautiously added. The benzene layer was separated and discarded and the water solution extracted with chloroform. The extract was evaporated to small bulk and treated with three times its volume of ether. A yellow oil at once separated and quickly solidified to a pale yellow powder. This was filtered and crystallized from methyl ethyl ketone.[19] In this manner 30 g. of white crystals was obtained, a yield of 66%. They were very soluble in water, alcohol and chloroform, slightly soluble in acetone, but insoluble in ether. If the compound was allowed to stand in moist air or was recrystallized from wet solvents, it took up water to form a dihydrate. A sample crystallized from a little water gave the same compound. This became completely anhydrous after heating for half an hour at 100° in air.

TABLE I

TRIPHENYL SELENONIUM SALTS. $(C_6H_5)_3Se— = R$

Salt	Formula	Decomp. temp.,[a] °C.	Selenium,[b] % Calcd.	Selenium,[b] % Found	Acidic element, % Calcd.	Acidic element, % Found	Solvent for crystallization
Chloride	RCI	230	22.87	22.44	10.26	10.32	MeCOEt
Chloride dihydrate	$RCl \cdot 2H_2O$	...[c]	...	...	9.28	9.23[d]	Water
Bromide[e]	RBr	236	20.29	20.09	20.45	20.51	MeCOEt
Iodide[f]	RI	237.5	18.11	18.05	29.06	29.31	Water
Dichromate	$R_2Cr_2O_7$	238	...	...	12.44	12.50	Dilute HAc
Picrate	$RC_6H_2N_3O_2$	...[g]	14.71	14.84	...	...	Alcohol
Nitrate[h]	RNO_3	...[i]	21.26	21.06	...	...	MeCOEt

[a] All temperatures are corrected. [b] Determined by the method of Shaw and Reid, THIS JOURNAL, 49, 2330 (1927). [c] Begins to lose water at about 82° in air. [d] Percentage loss of two molecules of water at 100°: calcd., 9.43; found, 9.32. [e] Prepared by dissolving the chloride in boiling ethylene bromide. On cooling, the bromide separates out. [f] On exposure to light, the white iodide slowly turns yellow. [g] M. p., 141–142°. [h] Separates from concd. water solution on addition of concd. nitric acid. [i] M. p. 107–108°.

Thermal Decomposition of the Triphenylselenonium Halides.—On heating the iodide to its melting point, a rather violent boiling took place and on cooling the substance remained liquid. This liquid was separated by fractionation into a substance boiling at 180–190° and another boiling at 295–302°. The first fraction was proved to be iodobenzene (b. p. 185°) by conversion into phenyl iodoso chloride. This was further checked by a mixed melting point with a known sample of phenyl iodoso chloride. The second fraction was identified as diphenyl selenide (b. p. 302°) by conversion into

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[19] The ketone was dried over anhydrous copper sulfate, as suggested by Locke, *Ind. Eng. Chem.*, 16, 956 (1924).

diphenylselenium dibromide, the identity of which was confirmed by a mixed melting point with some known diphenylselenium dibromide.[20]

In an entirely similar manner, triphenylselenonium bromide yielded two liquids boiling at 153–156 and 300–304°. The last was obviously diphenyl selenide, the first, bromobenzene (b. p. 156°). The chloride gave the selenide and a liquid boiling at 130–140°, which appeared to be chlorobenzene (b. p. 132°).

Summary

1. A method has been described for the synthesis of triphenylselenonium chloride, $(C_6H_5)_3SeCl$, by the action of benzene upon diphenylselenium dichloride in the presence of aluminum chloride.

2. From triphenylselenonium chloride the following salts have been prepared by metathesis: the bromide, iodide, dichromate, picrate and nitrate. Triphenylselenonium hydroxide appears to be a base of moderate strength.

3. The chloride, bromide and iodide have been shown to decompose with heat to give diphenyl selenide and chloro-, bromo- or iodobenzene, respectively.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

THE BROMINATION OF DESYLACETOPHENONE

BY CHARLES F. H. ALLEN AND ERNEST F. HERRMANN

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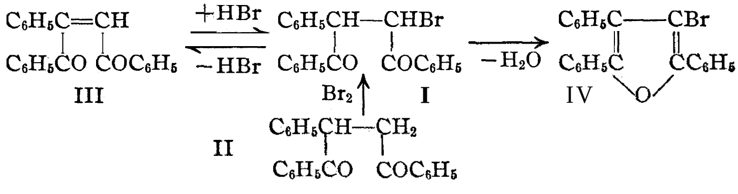
In an earlier paper[1] in which it was shown that bromofurans are produced when diacylstyrenes are treated with hydrogen bromide, the assumption was made that an open-chain addition product containing bromine was an intermediate product. Such a substance could form the ring compound by a loss of water from its enolic modification. Although the reaction undoubtedly took this course, unfortunately we were unable to isolate this bromo ketone (I)



In an attempt to prepare the latter substance, desylacetophenone (II), the saturated diketone corresponding to phenyldibenzoylethylene (III), was treated with bromine. In both chloroform and acetic acid solutions a quantitative yield of the bromofuran (IV) was obtained. Since the pri-

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[20] Krafft and Vorster, Ber., 26, 2818 (1893).

[1] Allen and Rosener, THIS JOURNAL, 49, 2110 (1927).

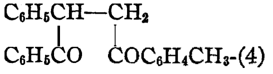
mary reaction was one of substitution, as evidenced by the copious evolution of hydrogen bromide, it was indicated that such a bromo ketone was undoubtedly formed. The closing of the ring doubtless was brought about by the dehydrating action of the hydrogen bromide. Acting upon this assumption, the bromination was carried out in acetic acid solution in the presence of a large amount of potassium acetate, a reagent which has previously been shown to be efficacious in removing hydrogen bromide as rapidly as formed.[2] Under these conditions and using small amounts it was found possible to isolate an open-chain bromo ketone (I) from the mixture. It was found that if large quantities were used, most of the product was the bromofuran, even when a considerable excess of potassium acetate was present. Evidently the acetic acid, acting as a dehydrating agent on a part of the bromo ketone first formed, brought about ring closure during the slow bromination.

We hoped that by selecting a solvent such as ethyl acetate, which was not a dehydrating agent, and using a limited amount of hydrogen bromide, it might be possible to isolate the open-chain bromo compound, starting with phenyldibenzoylethylene. This procedure was unsuccessful, a nearly quantitative yield of bromofuran being obtained.

On treatment with dehydrating agents the open-chain bromo compound loses the elements of water and forms the bromofuran (IV). Alcoholic potash, however, removes hydrogen bromide with consequent production of phenyldibenzoylethylene (III). The relation between these various compounds is shown in the outline above.

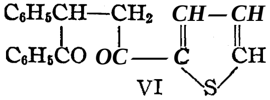
Experimental

The desylacetophenone was made by Smith's method.[3] Two homologs, using P-methylacetophenone and methyl *α*-thienyl ketone, were also prepared in the same way.



$$\begin{array}{ll} C_6H_5CH & -CH_2 \\ | & | \\ C_6H_5CO & COC_6H_4CH_3\text{-}(4) \end{array}$$

V



VI

	Substance	M. p., °C.	Calcd. C	Calcd. H	Found C	Found H
V	$C_{23}H_{20}O_2$	122	84.1	6.1	83.8	6.3
VI	$C_{20}H_{16}O_2S$	126	75.0	5.0	74.8	5.2

Bromination.—Five grams of desylacetophenone was dissolved in 25 cc. of warm glacial acetic acid, a little of the solution transferred to a test-tube and 3.1 g. of pulverized dry potassium acetate added to the remainder, the whole being in a flask fitted with a stirrer, condenser and dropping funnel, the end of which was drawn out into a fine capillary. A little bromine was added to the sample in the test-tube, and once hydrogen bromide was evolved the whole was introduced into the flask. A solution of 2.5 g. of bromine in 6 cc. of acetic acid was admitted, drop by drop, while stirring vigor-

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[2] Kohler, Graustein and Merrill, This Journal, **44**, 2549 (1922).

[3] Smith, J. *Chem. Soc.*, **57**, **649** (1890).

ously and refluxing in bright sunlight. The red bromine color was still present after boiling for two and a half hours. The mixture was poured into 200 cc. of water containing 5 g. of sodium bisulfite and the oily gum formed removed. The accumulated product from several runs was combined and after a tedious process of fractional crystallization, an open-chain bromo compound (I) and unchanged desylacetophenone (II) were separated in crystal form, The average yield of solid from several runs was 50%, only half of which was the desired bromine compound.

1,2,4-Triphenyl-3-bromobutandione-1,4 (I) crystallizes in long white needles that melt at 119° and decompose at 130°. It is readily soluble in all the usual organic solvents exsept petroleum ether.

Anal. Calcd. for $C_{22}H_{17}O_2Br$: Br, 20.4. Found: Br, 20.2.

When 30 g. of ketone was brominated in a similar way, the only solid containing halogen that could be isolated was 2,3,5-triphenyl-4-bromofuran (IV). This was doubtless owing to the dehydrating action of the acetic acid on the open-chain bromoketone, since it took several hours to add all the bromine.

Bromination in both chloroform and acetic acid in the absence of potassium acetate gave practically quantitative yields of the bromofuran. Thus 5 g. of desylacetophenone in 25 cc. of hot chloroform reacted instantly with the calculated amount of bromine in the same solvent, with copious evolution of hydrogen bromide. After evaporating about one-half and washing with sodium bisulfite, addition of two volumes of methyl alcohol caused the bromofuran to crystallize. This was filtered and a further amount obtained by partial evaporation of the filtrate. The total amount was 5 g. or 85%; it was identified as triphenylbromofuran by comparison with an authentic specimen.

The difference in the results of the two methods indicates that the hydrogen bromide formed must be involved in some way. Since it is known to accelerate the rate of enolization of ketones and because bromine combines rapidly with enolic forms in the absence of potassium acetate, the apparent substitution reaction is much faster; part of the hydrogen bromide may act as a dehydrating agent on the bromo ketone, which by loss of water forms the bromofuran. In the absence of hydrogen bromide, bromination is so slow that other reactions take place, accounting for the large amount of oily product and small amount of bromo ketone. If the treatment with bromine was prolonged until all of the desylacetophenone had disappeared, then the bromofuran appeared, formed by dehydration of the open-chain compound.

Hydrogen Bromide on Phenyldibenzoylethylene in Ethyl Acetate.—To 2 g. of phenyldibenzoylethylene in 25 cc. of hot ethyl acetate was added 2 g. of hydrogen bromide gas and the yellowish solution allowed to evaporate in a current of air. The only product was the bromofuran.

Alcoholic Potash on the Open-Chain Bromo Ketone.—Two-tenths gram of bromo ketone was added to 10 cc. of hot alcoholic potash; it rapidly dissolved. After five minutes the solution was cooled and acidified with acetic acid; 0.14 g. of yellow crystals of phenyldibenzoylethylene (III) slowly separated and was identified by comparison with an authentic specimen. The bromofuran is unaffected by prolonged boiling with alkalies.[1]

Dehydrating Agents on the Bromo Ketone.—A solution of 0.2 g. of bromo ketone in 10 cc. of glacial acetic acid was refluxed for two hours, poured into water and the precipitated gum taken up in a small amount of chloroform. On adding two volumes of alcohol, white, fluffy needles of the bromofuran crystallized in a quantitative yield. Acetic anhydride acted in a similar manner.

This work has been assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences,

Summary

1. Desylacetophenone reacts with bromine to form a monosubstitution product, which can be isolated only if the reaction is carried out in the presence of potassium acetate. In the absence of the latter reagent, ring closure takes place with formation of triphenylbromofuran.
2. The structure of the bromo ketone has been determined.

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THE MOLECULAR WEIGHT OF BENCE-JONES PROTEIN

By The Svedberg and Bertil Sjögren

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Certain diseases, especially myelomas, are characterized by the appearance in the urine of a peculiar protein called after its discoverer Bence-Jones protein.[1] The question of the origin of this abnormal product of cell life has caused much discussion. The comparative rareness of cases which are accompanied by the appearance of this protein has hampered the study of its properties. Recently such a case was reported from the Academic Hospital in Upsala and by courtesy of Professor G. Bergmark we received a sufficient quantity of urine for an ultracentrifugal investigation. In view of the fact that one of the theories about the origin of Bence-Jones protein considers it to be a product of protein cleavage, the determination of its molecular weight seemed to us to be of great interest. From analytical data Cohn has calculated a minimal molecular weight of 24,500,[2] but judging from the results of similar. computations compared with the results of ultracentrifugal determinations no certain conclusion as to *the actual molecular weight in aqueous solution* can be drawn from his calculation.

Preparation of Material.—To 2400 cc. of urine were added 4800 cc. of saturated ammonium sulfate solution and some toluene as a preservative. After standing for twenty-four hours at 0° the precipitate was centrifuged off and washed repeatedly with a mixture of two parts of saturated ammonium sulfate and one part of water. The precipitate was then dissolved in the smallest possible volume of water and reprecipitated with ammonium sulfate solution to a saturation degree of 60%. After standing for twenty-four hours at 0°, the precipitate was filtered off and washed with ammonium sulfate solution of 60% saturation. This material was divided in two parts. One portion was dissolved in phosphate buffer of P_H 5.5 (0.095 *M* in KH_2PO_4 and 0.005 *M* in Na_2HPO_4) and dialyzed at 0° against the same buffer for six days, after which time the SO_4-reaction was negative; volume of solution, 50 cc., concentration 1.19% (Ma-

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[1] See Wells, "Chemical Pathology," Saunders Co., Philadelphia and London, 5th ed., 1925, p. 596.

[2] Cohn, Hendry and Prentiss, *J. Biol. Chem.*, 63, 764 (1925).

terial I). A second portion was dialyzed against pure water and then electrodialyzed. No precipitate was formed during the electrodialysis. The concentration of this solution was 1.28% and the volume 200 cc. (Material II).

The isoelectric point of Material II was measured by A. Tiselius in this Laboratory and found to be 5.18. In electrochemical respects, therefore, Bence-Jones protein is distinctly different from egg albumin and serum albumin, which have isoelectric points at PH 4.6 and 4.9, respectively (according to recent determinations by Tiselius).

Specific Volume.—The partial specific volume was determined pycnometrically at 19.8°, as described in previous communications.[3] The data are shown in Table I.

TABLE I

PARTIAL SPECIFIC VOLUME OF BENCE-JONES PROTEIN AT 19.8°

Protein concn., %	Solvent	PH of soln	Partial spec vol.
0 80	0 006 M in HAc, 0.014 M in NaAc	5.0	0 747
1.19	0 006 M in HAc, 0 014 M in NaAc	5 0	749
1.32	Pure water	5.1	.751

These specific volumes are identical within the limits of error. The mean value 0.749 is also identical with the specific volumes of egg albumin, hemoglobin, serum albumin, serum globulin, phycocyan, phycoerythrin and edestin. As previously pointed out, this indicates a close relationship between all these proteins.[4]

Light Absorption.—The light absorption of solutions of Bence-Jones protein at various hydrogen-ion concentrations was measured with the Judd–Lewis spectrophotometer. Material II (electrodialyzed) was used and the measurements were carried out directly after making up the solutions. At the isoelectric point determinations were made in concentrations 0.06 and 0.12%, using a tube length of 2.0 cm. and in the concentration of 0.95% with 0.1-cm. tube length. All other determinations were performed on solutions of 0.05 and 0.10% using a tube length of 2.0 cm.

TABLE II

LIGHT ABSORPTION OF SOLUTIONS OF BENCE-JONES PROTEIN

Solvent					Wave length of maximum, $\mu\mu$	Wave length of minimum, $\mu\mu$	ϵ/c at maximum
	M		M	PH of soln.			
KCl	0.093	HCl	0.007	2.18	278	255	15.0
HAc	.017	NaAc	.003	3.94	278	253	13.0
HAc	.006	NaAc	.014	5.00	280	253	13.0
KH_2PO_4	.002	Na_2HPO_4	.031	7.74	280	252	13.0
Na_2HPO_4	.032	NaOH	.002	9 4 0	276	254	14.4
Na_2HPO_4	.050	NaOH	.008	10 85	278	255	17.0
Na_2HPO_4	.013	NaOH	.030	12.15	276	254	18.7
Na_2HPO_4	.010	NaOH	.036	12.45	278	255	18.7
NaOH	.05	NaCl	1%	12.66	276	256	18.6

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[3] Svedberg and Chirnoaga, THIS JOURNAL, 50, 1401 (1928).

[4] Svedberg and Sjögren, *ibid.*, 50,3321 (1928).

In Table II the positions of the maximum and the minimum of absorption and the extinction coefficients for the maximum are recorded. Figure 1 shows the absorption curves for three different hydrogen-ion concentrations.

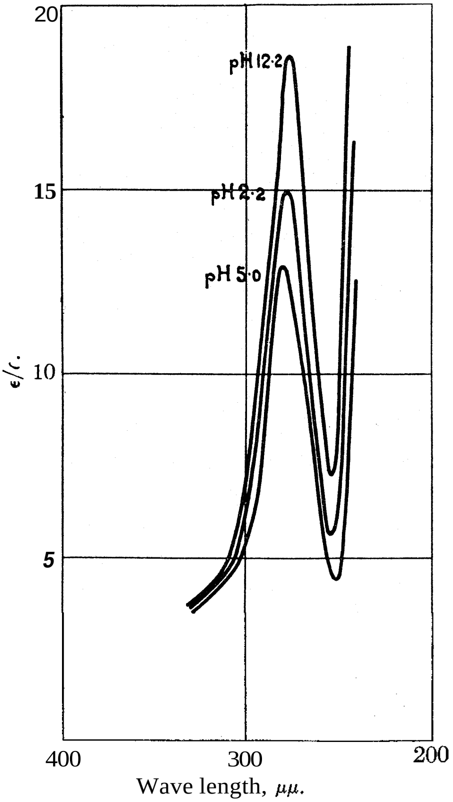

Fig. 1.

The position of the maximum and the minimum of the absorption curve is independent of *P*H. The value of the extinction is independent of *P*H within the region 3.94 to 7.74. In more acid and more alkaline solution, the extinction increases, indicating changes in the protein molecule. As will be seen from the molecular weight determinations, the molecule begins to break up into smaller units in the same *P*H regions where the light absorption begins to rise. There is a distinct difference however between the acid and the alkaline hydrolysis. The rise in light absorption on the acid side is caused by the formation of strongly absorbing noncentrifugible decomposition products, the mass of the centrifugible substance remaining unchanged, while the rise in light absorption on the alkaline side is due to the formation of centrifugible decomposition products.

Determination of Molecular Weight

Sedimentation Equilibrium Method.—A number of runs were made at different hydrogen-ion concentrations in order to determine not merely the molecular weight but also the stability region of the protein. As shown in previous communications[5,6] the molecular weight is given by the relation

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\omega^2 (x_2^2 - x_1^2)}$$

where R is the gas constant, T the absolute temperature, V the partial specific volume of the solute, ρ the density of the solvent, ω the angular

[5] Svedberg and Fåhraeus, THIS JOURNAL, **48, 430** (1926).

[6] Svedberg and Nichols, *ibid.*, **48**, 3081 (1926).

velocity and c_2 and c_1 the concentrations at the distances x_2 and x_1 from the center of rotation.

An improved type of ultracentrifuge for medium speed was used for these determinations. The cells employed were made as follows: an ebonite plate **25** mm. in diameter and with a sectorial aperture of **5°** cut from the periphery down to **7.5** mm. from the center of the plate was coated with a solution of rubber in benzene and after drying for a few minutes covered with two quartz plates of the same diameter and 5-mm. thick and slid into an ebonite collar. The latter was in its turn introduced into a steel collar threaded at the ends. By means of two steel guard rings and thin intermediate ebonite rings the quartz plates were firmly pressed together. Both the ebonite and the steel collar had openings coincident with the opening of the sectorial cell. The opening could be closed by an ebonite lid. Four different thicknesses were used for the ebonite middle plates, *viz.*, *2*, 4, ***8*** and 16 mm., giving the corresponding four thicknesses of solution and thus permitting a wide range of different concentrations to be studied. This new type of cell has proved to be more reliable than the cemented one previously described.[7] The ebonite sector plates do not crack as the glass or quartz sector plates often do when exposed to the centrifugal force, the cell is easier to clean and the rubber is more resistant to salt solutions than the de Khotinsky cement. The ebonite collar around the quartz plates protects them from uneven strain.

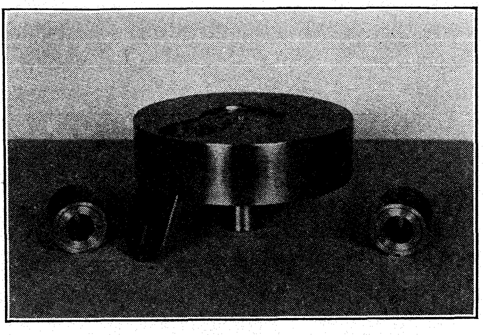

Fig. *2*.

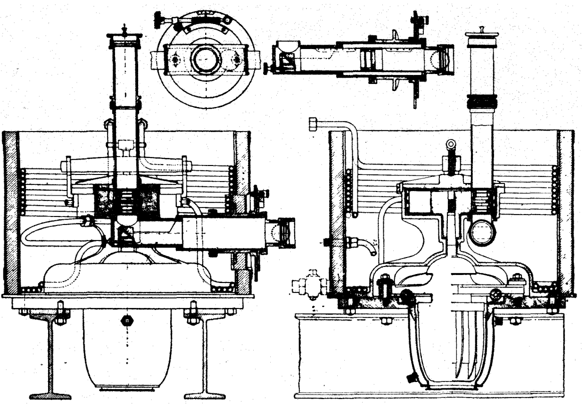

Fig. 3.

By choosing the inner diameter of the cell smaller, a thicker steel collar could be used which was less easily deformed by the centrifugal force. Optically the cell was defined by two steel diaphragms with sectorial apertures of **3°**, one on each side of the cell. The rotor was a chromium–nickel steel cylinder **15** cm. in diameter and 4 cm. thick and was arranged to receive two cells. One of them was used for the solution to be studied; the other was

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[7] Svedberg and Heyroth, THIS JOURNAL, 51, **552 (1929).**

filled with a non-centrifugible solution for standardizing the intensity of the illuminating lamp. Figure 2 shows the rotor with the two cells and one of the sector diaphragms removed. The rotor was supported upon a vertical steel shaft directly connected to the rotor of a special electric three-phase motor. The speed could be varied from 12,000 r.p m. down to about 2000 r.p.m. by varying the frequency of the current feeding the motor. The centrifuge rotor as well as the rotor of the electric motor was surrounded by hydrogen of atmospheric pressure confined within a casing about the moving parts of the centrifuge. To further ensure constant temperature, the stator of the motor was water-cooled and the casing within which the centrifuge rotor moved was immersed in a water thermostat. Freedom from vibration was ensured by a special circular rubber support for the stator. Suitable arrangements for passing of the light beam through the centrifuge and for taking exposures were made. Figure **3** gives a diagram of the centrifuge and Fig. 4 a photographic view of the whole apparatus except the camera. The latter (Fig. **5)** was placed in a room above the one where the centrifuge was mounted. The optical system used was about the same as previously employed? In Fig. 4 the water-cooled house for the mercury lamp can be seen to the right, then the light filter and the centrifuge follow from right to left. The horizontal illuminating beam is reflected vertically through the centrifuge by a quartz prism. Above the centrifuge is the photographic lens and part of the **camera.** On the wall are mounted the controlling instruments.3

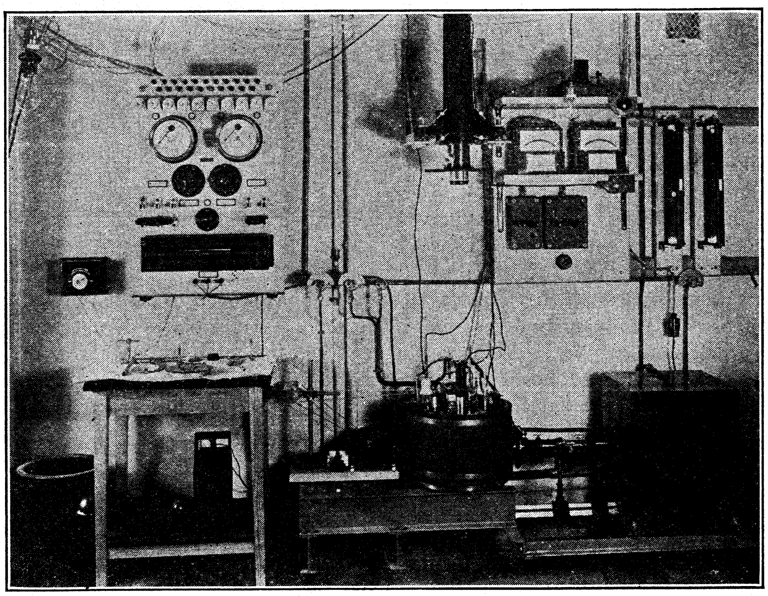

Fig. 4.

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[8] Svedberg and Heyroth, THIS JOURNAL, **51,553** (1929).

[9] The motor and the generator for the variable three-phase current were delivered by Siemens, Berlin; most of the other parts of the equipment were manufactured in the workshops of the laboratory.

For the runs described below a wave length range 290–240$\mu\mu$ was isolated from the mercury arc by means of bromine and chlorine light filters.

In Table III the results of a typical run are given and in Table IV are collected the main data of all the runs.

Within the PH region 3.94 to 7.74, the molecular weight is independent of the hydrogen-ion concentration, with a mean value of 35,000 ± 1000. The constancy of the molecular weight as a function of distance from center of rotation shows that the Bence-Jones protein is homogeneous with regard to molecular weight within the same PH region. At a PH of 10.85 considerable decomposition has taken place, the values of the molecular weight ranging from 36,100 (the normal weight) to 16,400. An attempt was made to determine the molecular weight at PH 12.66 (0.05 *M* in NaOH, 1% in NaCl) but during the long time required for reaching equilibrium, the light absorption increased enormously, indicating very strong hydrolysis. A sedimentation velocity run performed at the same PH, which required only six hours of centrifuging, indicated a molecular weight of about one-half that of the normal protein.

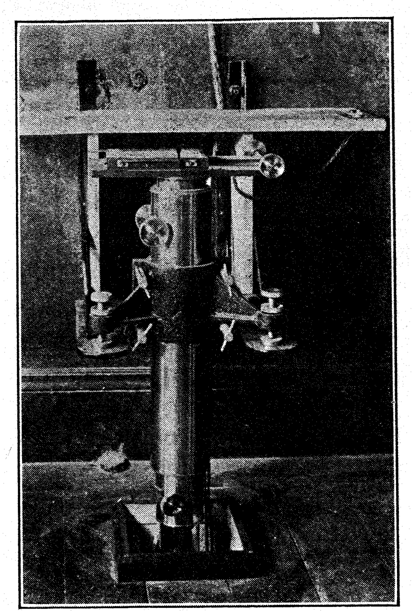
Fig. 5.

TABLE III

BENCE-JONES PROTEIN, SEDIMENTATION EQUILIBRIUM RUN

Concn., 0.05%; phosphate buffer, PH 5.5 (0.095 M in KH_2PO_4 and 0.005 M in Na_2HPO_4); V, 0.749; ρ, 1.006; T, 293.3; length of col. of soln., 0.525 cm.; thickness of col., 0.80 cm.; dist. of outer end of soln. from axis of rotation, 5.95 cm.; speed, 10,300 r.p.m. ($\omega = 343.3\pi$); standard, K_2CrO_4 $M/500$; source of light, mercury lamp; light filters, chlorine and bromine; aperture of objective, F:36; plates, Imperial Process; time of exposure, 45, 90 and 120 sec.; exposures made after 40, 45 and 51 hours of centrifuging.

Distances, cm. x_2	x_1	Mean concn., % c_2	c_1	Number of exposures	Mol. wt.
5.83	5.78	0.069	0.061	5	36,100
5.78	5.73	.061	.054	9	36,000
5.73	5.68	.054	.048	10	35,100
5.68	5.63	.048	,043	10	33,100
5.63	5.58	.043	.0382	10	35,500
5.58	5.53	.0382	.0342	10	34,600
5.53	5.48	.0342	.0305	10	34.700
				Mean	35,000

TABLE IV

BENCE-JONES PROTEIN, SUMMARY OF SEDIMENTATION EQUILIBRIUM MEASUREMENTS

Speed 10,000–11,000 r.p.m.

Solvent					Concn. of protein at	
	M		M	PH of soln.	start, %	Mol. wt.
HAc	0.017	NaAc	0.003	3.94	020	33,500
HAc	.006	NaAc	.014	5.08	.20	35,700
KH_2PO_4	.095	Na_2HPO_4	.005	5 50	.05	35,000
KH_2PO_4	.003	Na_2HPO_4	.031	7.74	.05	35,900
Na_2HPO_4	.050	NaOH	.008	10.85	.10	from 36.100
						to 16,400

Sedimentation Velocity Method.—For the sedimentation velocity runs the high-speed oil turbine ultracentrifuge previously described[10] was used. New cells of a somewhat different type resembling those described above for the new medium-speed ultracentrifuge were employed.

For most of the runs light of the wave length region 290–240$\mu\mu$ was isolated from the mercury arc by means of bromine and chlorine filters. Using a 12-mm. cell the lowest concentration of protein that could still be studied with this illumination was 0.10%. In order to render possible the study of still lower concentrations, a cadmium spark lamp was constructed. It was fed by a 1-kilowatt transformer giving 25,000 volts with a condenser parallel to the spark. An image of the spark in natural size was thrown on a small diaphragm by means of a quartz condenser and a slightly converging beam of light was then sent through the centrifuge by means of a second quartz lens possessing a focal length double that of the quartz condenser. By using a chlorine filter of 100 cm. a wave length region 231–214$\mu\mu$ could be isolated from the light given off by the spark. As demonstrated by the curves in Fig. 1, the light absorption of the protein is much higher in this wave length region. As a matter of fact, concentrations down to 0.025% could be studied by means of the cadmium spark lamp in combination with the 100-cm. chlorine filter.[11]

In the steady state of sedimentation the centrifugal force per mole of protein, $M(1 - V\rho)\omega^2 x$, and the frictional force per mole, $f dx/dt$, where f is the molar frictional constant and the other symbols have the same significance as previously, are equal. If we define $s = dx/dt\ 1/\omega^2 x$ as the specific sedimentation velocity or sedimentation constant, we have

$$M = \frac{fs}{1 - V\rho}$$

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[10] Svedberg and Nichols, THIS JOURNAL, 49, 2920 (1927); Svedberg, "Colloid Chemistry," 2d ed., Chemical Catalog Co., New York, 1928, p. 153.

[11] No bromine filter was used in this case because the light absorption of bromine is too high in the very short waved ultraviolet region. One of the functions of the long chlorine filter is that of absorbing the violet light.

If we assume that the molar frictional constant effective in sedimentation is the same as the one effective in free diffusion we are justified in using the relation $f = RT/D$, where D is the diffusion constant, and thus get for the molecular weight[10]

$$M = \frac{RTs}{D\,(1 - V\rho)}$$

The fact that in most cases hitherto studied the values of the molecular weights obtained by the sedimentation equilibrium and the sedimentation velocity method check within the limits of experimental error (hemoglobin, serum albumin, serum globulin, phycocyan, phycoerythrin, edestin) demonstrates that the above assumption is as a rule justified. Certain exceptions have been observed however. For hemocyanin the diffusion as measured from the sedimentation pictures was abnormally low at higher concentrations but became normal at high dilutions from about $^1/_3\%$ downward.[12] The sedimentation constant was only slightly affected by the forces which at higher concentrations depressed the diffusion. A similar effect has been observed for cellulose.[13] Recently several instances of abnormal diffusion persisting down to very low concentrations have been observed. In such cases the sedimentation velocity has always been perfectly in line with the molecular weight obtained from sedimentation equilibrium measurements. From these facts we must draw the conclusion that the value of the molar frictional constant derived from the diffusion formula where a perfectly free movement of the molecules is assumed is not necessarily the same as the molar frictional constant which is effective in the sedimentation of molecules in a field of force. In the latter case the molecules need not move independently of each other.

The determinations of sedimentation constant and diffusion constant for Bence-Jones protein have shown that the values of the diffusion constant are irregular and abnormally low even down to a few hundredths of a per cent. On the other hand, the values of the sedimentation constant were quite regular. In the following, therefore, only these latter determinations will be mentioned.

In order to explore the PH stability region more in detail than was done by the equilibrium measurements, a series of determinations of the sedimentation constant was performed at different hydrogen-ion concentrations. The solutions were brought to the desired concentration and PH immediately before starting the runs. In Table V the results are summarized. Figure 6 shows the relation between sedimentation constant and PH graphically. In the same diagram are plotted the values of the extinction coefficient at the maximum of absorption as function of PH. In the *PH* region 3.5–7.5, both sedimentation and light absorption are practi-

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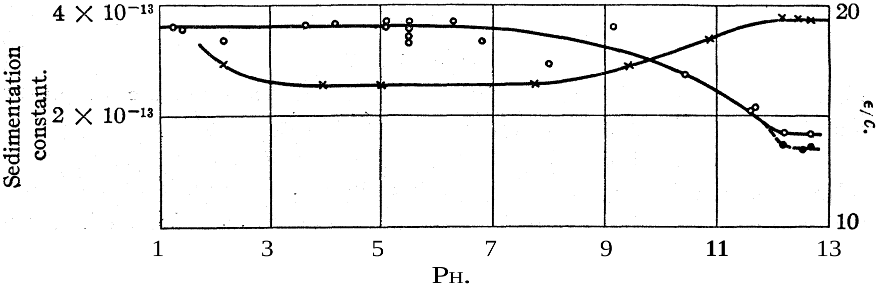
[12] Svedberg and Chirnoaga, THIS JOURNAL, 50,1399 (1928).

[13] Stamm, unpublished investigations.

cally constant and no non-centrifugible substance is formed. The protein is very stable in this *P*H region. At lower PH values the light absorption increases, while the sedimentation constant remains unchanged. The photograms of the solution during centrifuging indicate that at PH values of 1.2–1.4, 40–35% of the protein is broken up into a non-centrifugible substance. This accounts for the rise in light absorption. At the acid



○, Sedimentation constant; ×, ε/c.

Fig. 6.

TABLE V

BENCE-JONES PROTEIN, SUMMARY OF SEDIMENTATION VELOCITY MEASUREMENTS

Time of centrifuging, 4 to 6 hours. Speed, 42,000–47,000 r.p.m.

Solvent	*M*		*M*	PH of soln.	Concn. of protein, %	$s_{20} \times 10^{13}$
HCl	0.1	KCl	0.1	1.2	0.05	3.60
HCl	.04	KCl	.16	1.4	.06	3.56
HCl	.007	KCl	.093	2.15	.08	3.34
HAc	.018	NaAc	.002	3.63	.12	3.67
HAc	.015	NaAc	.005	4.20	.12	3.69
HAc	.006	NaAc	.014	508	.10	3.65
Pure water				5.10	.12	3.70
KH_2PO_4	.095	Na_2HPO_4	.005	5.5	.025[a]	3.43
KH_2PO_4	.095	Na_2HPO_4	.005	5.5	.10	3.71
KH_2PO_4	.095	Na_2HPO_4	.005	5.5	.78	3.63
KH_2PO_4	.095	Na_2HPO_4	.005	5.5	1.00	3.39
KH_2PO_4	.080	Na_2HPO_4	.020	6.30	0.12	3.42
KH_2PO_4	.050	Na_2HPO_4	.050	6.82	.12	3.35
KH_2PO_4	.005	Na_2HPO_4	.095	8.00	.11	2.94
Na_2HPO_4	.032	NaOH	.001	9.14	.12	3.64
Na_2HPO_4	.026	NaOH	.012	10.47	.060	2.79
Na_2HPO_4[b]	.050	NaOH[b]	.025	11.61	.055	2.13
Na_2HPO_4	.017	NaOH	.025	11.69	.055	2.17
Na_2HPO_4	.013	NaOH	.030	12.15	.045	1.49
Na_2HPO_4[b]	.013	NaOH[b]	.030	12.23	.04	1.69
		NaOH	.05	12.60	.04	1.40
Na_2HPO_4	.003	NaOH	.044	12.61	.04	1.44
NaOH[b]	.05			12.66	.04	1.69

[a] Cadmium light was used. [b] 1% in NaCl.

side, therefore, the molecule is directly hydrolyzed into small molecules and what still remains of bigger molecules shows the normal sedimentation of the protein. At PH values higher than 7.5 the light absorption increases while the sedimentation constant decreases. Both curves have a small horizontal **part** in the *PH* region 12.2–12.7 indicating that the centrifugible part of the protein has reached a second stability range. An increasing amount of non-centrifugible substance is being formed, amounting to about 18% at PH 12.7. As an average value of 13 determinations of the sedimentation constant within the stability region including the isoelectric point we get 3.55×10^{-13}. Some of the determinations at high PH values show a marked Donnan effect. While the two runs at *PH* 11.61 and 11.69 gave practically the same sedimentation constant, 2.13 and 2.17, with and without 1% NaCl present, the runs from PH 12.15 show a marked salt effect. Without salt the values of the sedimentation constant are 1.49, 1.40 and 1.44, at the *PH* of 12.15, 12.60 and 12.61, while the values found in the presence of 1% NaCl are 1.69 and 1.69 at the PH of 12.23 and 12.66. The value 1.69 is probably free from any influence of the Donnan effect.

Discussion of Results

The ultracentrifugal study of Bence-Jones protein has shown this substance to be uncommonly stable. Within the *PH* range 3.5–7.5 there is no decomposition of the molecule The sedimentation equilibrium method has given a mean value of 35,000 for the molecular weight, determinations being made in the PH range 3.94–10.85. From *PH* 3.94 to 7.74 the protein was found to contain only molecules of weight 35,000. A run at PH 10.85 showed a drift in the values of the molecular weight from 36,100 at the bottom of the cell to 16,400 at the top of the cell. At this PH, therefore, the protein is a mixture. The sedimentation velocity runs have shown that in the PH region 1.2–3.5 there is hydrolysis of the molecule into a non-centrifugible substance. The remaining protein has the same sedimentation constant as in the PH region, where it is perfectly stable. In the PH region 7.5–12.2 the sedimentation decreases steadily. In the PH range 12.2–12.7 the sedimentation is constant. Now it is of considerable interest to notice that the molecular weight of 35,000 found for the Bence-Jones protein by means of the sedimentation equilibrium method is practically identical with the molecular weight found by the same method for egg albumin,[6] *viz.*, 34,500, and that the sedimentation constant found for the Bence-Jones protein within the stability region which includes the isoelectric point is 3.55×10^{-13}, while the same constant found by Nichols for egg albumin is 3.32×10^{-13}.

The molar frictional constant $f = [M(1 - V\rho)]/s$ for Bence-Jones protein at 20° is 2.48×10^{16} and for egg albumin 2.63×10^{16}. The molar frictional constant f_s for a substance of molecular weight 35,000 and possessing spherical molecules of the same specific volume as Bence-Jones protein can easily be calculated from the relation $f_s = 6\pi\eta N(3MV/4\pi N)^{1/3}$, where η is the viscosity of the solvent, N the Avogadro constant and the other symbols have their usual significance. The value is 2.49×10^{16}. The corresponding value for egg albumin is 2.47×10^{16}. The ratio f/f_s may be taken as measure of the dissymmetry of the molecule. For a spherical molecule this ratio should be unity. From our experimental data we find for Bence-Jones protein $f/f_s = 1.00$ and for egg albumin 1.06. The data at our disposal also permit of the calculation of the radius of these spherical molecules. By means of the formula $r = (3MV/4\pi N)^{1/3}$ we get for Bence-Jones protein $r = 2.18\mu\mu$ and for egg albumin $2.17\mu\mu$.

The normal Bence-Jones protein, therefore, seems to have molecules of the same weight as egg albumin. Both proteins have spherical molecules of a radius of about $2.2\mu\mu$. The molecular weight value for the lightest component in the equilibrium run at P_H 10.85 was 16.400, which is not far from one-half the weight of the undecomposed protein. The sedimentation constant value found at high P_H values in the presence of salt was 1.69, while the value to be expected for a molecule of one-half the weight of the normal Bence-Jones protein and having about the same degree of dissymmetry as the other dissymmetrical protein molecules so far studied in this Laboratory is 1.70. It therefore seems probable that at high P_H values the molecule of the Bence-Jones protein is split up into halves. At the same time an ordinary hydrolysis producing non-centrifugible substance begins.

From the pliysiological point of view it is of interest to observe that native egg albumin also to some extent passes normal kidneys, just as the Bence-Jones protein does, while the appearance of serum albumin in the urine is accompanied by some change in the function of the kidneys. Now serum albumin has the double molecular weight of egg albumin and Bence-Jones protein. It may be, therefore, that the appearance of one or the other of these proteins in urine is more or less a question of permeability.

The expenses connected with these experiments have been defrayed by grants from the foundation "Therese and Johan Anderssons Minne" and from the Nobel Fund of Chemistry.

Summary

1. The ultracentrifugal methods have been applied to the study of the molecular weight and P_H stability range of Bence-Jones protein.

2. In the P_H range 3.5–7.5 the protein is stable and has a molecular weight of 35,000 ± 1000, a sedimentation constant of 3.55×10^{-13} and

a molar frictional constant of 2.48 X 10^{16} (both at 20°); a comparison with the molar frictional constant calculated for a spherical molecule of the same molecular mass and volume shows that the molecule of Bence-Jones protein is spherical and has a radius of 2.18$\mu\mu$.

3. At PH values lower than 3.5 the molecule breaks up into some non-centrifugible substance, the remaining protein having the normal molecular weight. The acid hydrolysis of the protein is accompanied by a rise in light absorption.

4. At PH values higher than 7.5 a slight alkaline hydrolysis sets in, producing a non-centrifugible substance, but the main change brought about by the high ***PH*** is a splitting up of the molecule into a centrifugible substance which probably has a molecular weight equal to half that of the normal molecule. In the PH range 12.2–12.7 the sedimentation constant has a value of 1.69 X 10^{-13}. The light absorption increases in the ***PH*** range 7.5–12.2 and then becomes constant again.

5. A comparison between Bence-Jones protein and egg albumin with regard to molecular weight, sedimentation constant and molar frictional constant shows that the values are identical within the limits of experimental error. Although these two proteins are entirely different as to chemical composition and isoelectric point, their molecular mass and size are almost identical.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO ALKYL TIN COMPOUNDS. III. SOME PROPERTIES OF TRIMETHYL TIN HYDROXIDE

BY CHARLES A. KRAUS AND RALPH H. BULLARD

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Recently Kraus and Harada[1] have described compounds formed between trimethyl tin hydroxide and trimethyl tin halides corresponding to the formula $[(CH_3)_3SnOH]_2(CH_3)_3SnX$. In attempting to establish the constitution of these compounds, it was found necessary to study the properties of trimethyl tin hydroxide, and, particularly, its thermal decomposition. The present paper records the results of the latter investigation.

Preparation of $(CH_3)_3SnOH$.—According to Cahours,[2] trimethyl tin hydroxide is formed on treating trimethyl tin halides with a strong solution of an alkali. The hydroxide is readily soluble in water and sublimes at temperatures above 80°. Considerable difficulty was experienced in the preparation of the pure hydroxide, which was invariably accompanied by a large loss of material. As will be shown later, this loss was probably due

[1] Kraus and Harada, THIS JOURNAL, 47, 2416 (1925).

[2] Cahours, Ann., 114, 377 (1860).

to decomposition of the hydroxide at the higher temperatures. The following method of preparation was found to yield fairly satisfactory results.

Trimethyl tin bromide is introduced into a flask containing a 55% solution of sodium hydroxide (m. p. 40°) at a temperature just above its melting point. The flask is placed in a horizontal position in a sheet metal steam-bath with the neck projecting through an opening in one side. A closely fitting glass tube slipped over the neck of the flask outside the box serves as condenser. Sublimation is continued until droplets of moisture begin to appear on the walls of the condenser. The sublimate consists of practically pure trimethyl tin hydroxide containing a trace of moisture which is removed by means of ordinary drying agents in a desiccator. The yield is in the neighborhood of 75%.

Anal. Subs., 0.4297: SnO_2, 0.3065. Calcd. for $(CH_3)_3SnOH$: Sn, 65.69. Found: Sn, 66.08.

Thermal Decomposition of $(CH_3)_3SnOH$.—According to Cahours,[2] trimethyl tin hydroxide undergoes decomposition at higher temperatures according to the equation

$$2(CH_3)SnOH = [(CH_3)Sn]_2O + H_2O \qquad (1)$$

Our own experiments, to be described below, indicate that decomposition takes place according to the equation

$$2(CH_3)_3SnOH = (CH_3)_2SnO + (CH_3)_4Sn + H_2O \qquad (2)$$

This reaction, in all likelihood, takes place in two stages, as follows

$$2(CH_3)_3SnOH = [(CH_3)_3Sn]_2O + H_2O \qquad (3)$$

$$[(CH_3)_3Sn]_2O = (CH_3)_2SnO + (CH_3)_4Sn \qquad (4)$$

On attempting to sublime a quantity of the hydroxide at 200° in a tube placed in an electric furnace, practically no sublimate appeared, while a white residue was left behind in the tube. On analysis,[3] this residue was found to consist largely of dimethyl tin oxide.

Anal. Subs., 0.3161, 0.3328: SnO_2, 0.2922, 0.3072. Calcd. for $[(CH_3)_3Sn]_2O$: Sn, 69.13; for $(CH_3)_2SnO$: Sn, 72.05. Found: Sn, 72.81, 72.71.

A quantity of trimethyl tin hydroxide was placed in one leg of an inverted U-tube which was then evacuated and sealed. The limb containing the hydroxide was kept in boiling water for three days. The major portion of the hydroxide underwent decomposition. A distillate, consisting of two liquids, collected in the second leg. The less volatile of these proved to be water, while the more volatile was identified as tetramethyl tin, b. p. 77.5°. The residue in the first leg of the U-tube was washed with absolute alcohol to remove traces of undecomposed hydroxide and the resulting product was analyzed for tin.

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[3] The analyses were carried out according to a modification of the method of Krause, ***Ber.***, 55, 896 (1922). Krause oxidized the compounds by means of a mixture of sulfuric and nitric acids in a crucible. We have found it more advantageous to carry out the oxidation in pyrex tubes having a diameter of approximately 15 mm. and a length of from 15 to 20 cm. Under these conditions the chances of loss are very greatly reduced over the crucible method. In the case of certain compounds which are oxidized with extreme difficulty, fuming sulfuric and nitric acids are employed. In general, fuming acids are not required in the case of tin compounds, but they often are necessary in the case of germanium and silicon. With the use of a counterpoise, reproducible results were obtained with pyrex tubes. If extreme accuracy is required, silica tubes are preferable.

Anal. Subs., 0.1530, 0.1533: SnO_2, 0.1417, 0.1419. Calcd. for $(CH_3)_2SnO$: Sn, 72.05. Found: Sn, 72.95, 72.91.

The residue was dissolved in dilute hydrochloric acid and on evaporating there were recovered crystals melting at 107°; this identifies them as dimethyl tin dichloride, m. p. 108°. As is apparent from the above analysis, the tin content of the residual product was in all cases slightly higher than is required for dimethyl tin oxide. This discrepancy was probably due to partial decomposition of dimethyl tin oxide, as will be shown below. Trimethyl tin hydroxide evidently decomposes according to Equation 2. It is remarkable that, volatile as the hydroxide is, it is so largely decomposed at a moderate temperature. It is of interest to note that according to Chambers and Scherer,[4] triphenyl tin hydroxide decomposes at higher temperatures with the formation of diphenyl tin oxide and tetraphenyl tin.

Thermal Decomposition of Trimethyl Tin Oxide.—A quantity of trimethyl tin oxide, prepared by the oxidation of trimethyl tin,[5] was placed in one limb of an evacuated, inverted U-tube and heated to 120° in a paraffin-bath. A small quantity of liquid collected in the second limb of the tube which failed to freeze at liquid ammonia temperatures. The temperature of the paraffin-bath was then raised to 190° and maintained for some time. On opening the tube, the presence of a permanent gas was noted. The liquid formed in this reaction was identified as tetramethyl tin, b. p. 77.7°. The white residue in the first limb of the tube was analyzed for tin.

Anal. Subs., 0.2272, 0.2839: SnO_2, 0.2068, 0.2587. Calcd. for $(CH_3)_2SnO$: Sn, 72.05. Found: Sn, 71.69, 71.77.

The low value found for tin may have been due to a side reaction, as was indicated by the presence of a permanent gas. For the most part reaction proceeds according to Equation 4. When trimethyl tin hydroxide is heated, therefore, reaction, in all likelihood, first proceeds according to Equation 3, in which trimethyl tin oxide is formed; the latter compound, in turn, decomposes according to Equation 4.

Thermal Decomposition of Dimethyl Tin Oxide.—The high values obtained for tin in the residue left on decomposing trimethyl tin hydroxide suggested that dimethyl tin oxide is not completely stable under the conditions of these experiments. Accordingly, a quantity of dimethyl tin oxide was sealed in one leg of an evacuated U-tube, which was then heated with a free flame, while the other leg was cooled in ice water. A small quantity of liquid appeared in the second leg of the tube and was identified as tetramethyl tin. The residue in the first leg turned black while at the same time a gaseous pressure was built up in the tube. A quantity of this gas was collected and its density determined. The density corresponded to a mean molecular weight of 43.7. It was thought that this high value was due to the presence of tetramethyl tin. Therefore, in a second preparation, the gas was passed through a condenser cooled in liquid ammonia. The density of the resulting gas was found to correspond to a mean molecular weight of 26.5. This seemed to indicate that, while the methyl groups, in part, combined to form ethane, some of them interacted to form methane and ethylene. On passing the gas through a solution of potassium permanganate, the solution was immediately decolorized, indicating the presence of unsaturated hydrocarbons.

The tube used in the first preparation was evacuated and the material heated for some time to a temperature of about 400°. The black residue left behind was analyzed for tin.

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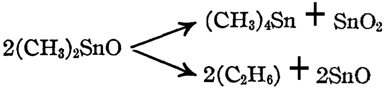
[4] Chambers and Scherer, THIS JOURNAL, 48, 1054 (1926).

[5] Kraus and Sessions, *ibid.*, 47, 2363 (1925).

Anal. Subs., 0.3714, 0.1291: SnO_2, 0.4022, 0.1396. Calcd. for SnO_2: Sn, 78.76; for SnO, Sn, 88.12. Found: Sn, 85.29, 85.23.

The analyses indicate that the mixture consisted of 30.5% of stannic oxide and 69.5% of stannous oxide. On heating dimethyl tin oxide, reaction for the most part takes place according to the equations



$$2(CH_3)_2SnO \rightarrow (CH_3)_4Sn + SnO_2$$
$$2(CH_3)_2SnO \rightarrow 2(C_2H_6) + 2SnO$$

The above experiments show that if trimethyl tin oxide is formed in the thermal decomposition from trimethyl tin hydroxide, it is immediately decomposed to dimethyl tin oxide and tetramethyl tin. At still higher temperatures dimethyl tin oxide is decomposed, a mixture of stannous and stannic oxides being left behind, while tetramethyl tin and hydrocarbons are evolved.

Molecular Weight of Trimethyl Tin Hydroxide in Benzene.—The molecular weight of the hydroxide was determined in benzene solution by the cryoscopic method. The results are given in Table I.

TABLE I

MOLECULAR WEIGHT OF $(CH_3)_3SnOH$ IN BENZENE

Benzene, g.	$(CH_3)_3SnOH$, g.	Δt	Mol. wt.
46.23	0.1460	0.072"	219
41.39	.1343	.073°	222

The formula weight of trimethyl tin hydroxide is 180.8. Apparently, the hydroxide is appreciably associated in benzene solution. This result is in agreement with observations of Smith and Kipping.[6] They determined the molecular weight of tribenzyl tin hydroxide in benzene at its freezing point and in chloroform at its boiling point. For the molecular weight they obtained the values 660 and 727–821 in these two solvents, respectively. The formula weight of tribenzyl tin hydroxide is 409. It seems, then, that the tertiary alkyl tin hydroxides have a marked tendency to polymerize when dissolved in solvents of this type.

Summary

A method is described for the preparation of trimethyl tin hydroxide. The apparent molecular weight of the hydroxide in benzene indicates that it is slightly polymerized.

At slightly elevated temperatures trimethyl tin hydroxide decomposes, dimethyl tin oxide, tetramethyl tin and water being formed.

Trimethyl tin oxide undergoes thermal decomposition with the formation of dimethyl tin oxide and tetramethyl tin. At elevated temperatures dimethyl tin oxide decomposes, in part, with the formation of ethane and stannous oxide and, in part, with the formation of stannic oxide and tetra-

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[6] Smith and Kipping, J. *Chem. Soc.*, 103, 2042 (1913).

methyl tin. Small quantities of methane and unsaturated hydrocarbons are also formed,

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THE COUPLING OF GLUCOSE AND GAMMA-FRUCTOSE. CONVERSION OF SUCROSE INTO ISO-SUCROSE

BY JAMES COLQUHOUN IRVINE AND JOHN WALTER HYDE OLDHAM

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From the theoretical standpoint the primary condition necessary for the synthesis of sucrose is to have in hand an equimolecular mixture of tetra-acetylglucose and tetra-acetyl-γ-fructose which can be subjected to the action of a dehydrating agent. In a previous paper[1] we have described the results obtained when the required y-form of tetra-acetylfructose was prepared both from fructose and from inulin but when the compound was condensed with tetra-acetylglucose the only crystalline product isolated by us was not the octa-acetate of sucrose but the corresponding derivative of a new disaccharide which we termed "iso-sucrose." This failure to synthesize sucrose octa-acetate cannot be attributed to faulty manipulation in the sense that traces of acids had decomposed any sucrose derivatives which had been formed. Nor can it be ascribed to the use of a fructose acetate containing an oxygen ring in a different position from that present in the fructose component of sucrose. In our former work we established, and have since confirmed, the fact that iso-sucrose is much more readily hydrolyzed by acids than sucrose itself, and the ready isolation of the less stable disaccharide is a guarantee that the more stable isomeride had not been decomposed. Lest it be maintained that the tetra-acetylfructose used by us was not the same y-form as is present in sucrose, we have now varied the procedure so as to ensure that this objection cannot apply.

When sucrose octa-acetate is acted on by acetyl bromide dissolved in glacial acetic acid, the disaccharide is ruptured into its components and the product consists of an equimolecular mixture of tetra-acetylglucose and tetra-acetyl-y-fructose. It might reasonably have been expected that such a mixture would represent the ideal starting material for the synthesis of sucrose, but all attempts to re-condense the constituents by the action of phosphoric anhydride have again resulted in the formation of crystalline iso-sucrose octa-acetate. As before, the reaction yielded syrupy acetates of disaccharides other than iso-sucrose and, on occasions, iso-trehalose octa-acetate was isolated, but despite numerous variations in procedure no evidence has been obtained of the formation of sucrose

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[1] Irvine, Oldham and Skinner, THIS JOURNAL, 51, 1279 (1929).

octa-acetate in this reaction. The series of changes may be summarized in the following scheme

$$\begin{tikzcd}
 & \text{Tetra-acetylglucose} \arrow[dr] & & \\
\text{Sucrose} \arrow[ur] \arrow[dr] & & \text{\textit{Iso}-sucrose octa-acetate} \arrow[r] & \text{\textit{Iso}-sucrose} \\
 & \text{Tetra-acetyl-y-fructose} \arrow[ur] & &
\end{tikzcd}$$

The above scheme has been supplemented by using tetra-acetyl-γ-fructose derived from an entirely different source.

It will be recalled[2] that a tri-acetylanhydrofructose may be obtained from inulin tri-acetate and we find that this compound when treated with acetyl chloride and dry hydrogen chloride is converted smoothly into tetra-acetyl-7-fructose showing the correct constants. The condensation of this tetra-acetyl-y-fructose with tetra-acetylglucose by the agency of phosphoric anhydride once more gave *iso*-sucrose octa-acetate melting at 130–131°. Incidentally, this result shows that, in all probability, tri-acetylanhydrofructose contains one oxygen ring in the γ-position, and in this respect resembles the remainder of the inulin molecule.

Experimental

Action of Acetyl Bromide on Sucrose Octa-acetate.—The correct conditions for carrying out this reaction were established only after a large number of trial experiments had been made in which the concentration of the reagent and the time of the reaction were varied over wide limits. Owing to the destructive action of hydrogen bromide on fructose derivatives it is advisable to arrest the change when not more than one-half of the sucrose octa-acetate has been hydrolyzed.

A 5% solution of sucrose octa-acetate in glacial acetic acid containing 15% of acetyl bromide was maintained at the temperature of the room; the optical rotation increased steadily in the dextro-sense and at the end of approximately fifty hours the reaction was arrested by cooling in ice, diluting largely with acetic acid and thereafter adding powdered ice with active stirring. When all or the acetyl bromide was decomposed a solution of sodium acetate was added in slight excess of that required to neutralize the hydrogen bromide and the mixture was then warmed at 60° for forty-five minutes. Blank experiments showed that this treatment converts acetobromoglucose quantitatively into tetra-acetylglucose.

The cold solution was then extracted six times with chloroform, the material extracted being isolated, dissolved in benzene and the benzene solution thereafter extracted with water. The aqueous extract contained the desired mixture of glucose and fructose tetra-acetates, while unaltered sucrose octa-acetate remained in the benzene.

TABLE I

DATA SHOWING THE RELATIVE YIELDS UNDER DIFFERENT CONDITIONS

Concentration of sucrose octa-acetate, 5%; of acetyl bromide, 15%

No.	Acetate g.	Duration of expt , hours	Final $[\alpha]_D$	Total prod., g.	Extracted by C_6H_6, g.	Extracted by Water, g.
I	50	67	+123.8°	43.9	16.9	23.9
II	50	43	+104.2°	48.5	27.5	19.2

The procedure of Experiment II was adopted as the most satisfactory practical method.

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[2] Irvine and Stevenson, THIS JOURNAL, 51, 2197 (1929).

Examination of the Mixed Acetates of Glucose and Fructose.—On extracting the aqueous solution with chloroform and subsequent removal of this solvent, the mixed acetates remained as a colorless, viscous sirup. The acetyl content was 48.6%; calcd., *49.3%;* in chloroform solution $[\alpha]_D = +58.0'$ for $c = 3.068$. From these results it is possible to calculate the relative proportions of tetracetyl-y-fructose and tetra-acetylglucose in the mixture. The activity of tetracetyl-7-fructose in chloroform shows slight variation but the average value for $[a]_D$ is $+34.5°$. Applying this figure the above mixture should contain

Tetra-acetyl-γ-fructose	49.2%
Tetra-acetylglucose	50.8%

This composition was confirmed. A weighed quantity of the mixture (about 0.5 g.) was dissolved in water containing a little acetone and, after cooling in ice, a slight excess of *2 N* sodium hydroxide was added. Twenty minutes later sufficient acid was added to make the solution approximately *N*/10 and the rotation was determined. Under the conditions specified the solution, which contained glucose and fructose, gave $[\alpha]_D = -17.7°$. Control experiments established that under the same conditions tetra-acetyl-γ-fructose gives the end-point $[\alpha]_D = -89.4°$, while that for tetra-acetylglucose is $[\alpha]_D$ +50.3°. It follows that the mixture of acetates under examination contained *48.57'* of tetra-acetyl-y-fructose as against *49.2%* determined by the direct method.

Condensation of the Hexose Acetates.—This was carried out by the action of phosphoric anhydride as previously described.' The total product of the condensation showed the usual reducing action on Fehling's solution and from the mixture iso-sucrose octa-acetate (m. p. 129–131° $[\alpha]_D$ in chloroform +19.3°) was the only crystalline compound obtained. The identity of this product with the iso-sucrose octa-acetate previously described by us was confirmed.

Conversion of Triacetylanhydrofructose into Tetra-acetyl-γ-fructose.—Seven and four-tenths grams of crystalline triacetylanhydrofructose was dissolved in *74* cc. of acetyl chloride saturated with dry hydrogen chloride. The solution was preserved at the temperature of the room for six weeks, the rotation being determined at intervals until the darkening of the liquid interfered with accurate reading. The initial value, $[\alpha]_D$ +4.3°, increased to the approximate maximum of $55 2°, at which stage the acetyl chloride was removed in a vacuum. On taking up the product in glacial acetic acid, powdered ice was added and thereafter water, the system being kept homogeneous if necessary by the addition of more acetic acid. After extensive dilution with water the liquid was extracted six times with chloroform and, on removal of the solvent and thorough drying of the residue at 100° in a vacuum, the product was taken up in benzene. When the benzene solution was extracted with water, unchanged tri-acetylanhydrofructose (weight = *1.8* g.) remained behind and *4.09* g. of tetra-acetyl-γ-fructose passed into the solution, from which it was isolated in the usual way. Found: CH_3CO, 50.0%; n_D *1.4652;* $[\alpha]_D$ in benzene +38.1° for c = *4.9%;* after alkaline hydrolysis in the cold, $[\alpha]_D$ calculated on the weight of hexose formed was *−89.0".* The corresponding values for tetra-acetyl-7-fructose prepared by other methods are: CH_3CO, 50.8% (calcd., 49.4%), n_D *1.4645;* $[\alpha]_D$ in benzene +38.7° for $c = 5.4\%$; specific rotation on cold alkaline hydrolysis *−89.4'.* No description of the condensation of this specimen of tetra-acetyl-γ-fructose with tetra-acetylglucose is necessary as the procedure and results were the same as in former experiments.

Summary

1. Sucrose octa-acetate has been converted into an equimolecular mixture of tetra-acetylglucose and tetra-acetyl-y-fructose.

2. This mixture when subjected to the condensing action of phosphoric anhydride has not yielded sucrose octa-acetate, the only crystalline product obtained being the octa-acetate of iso-sucrose.

3. Tri-acetylanhydrofructose has been converted into tetra-acetyl-γ-fructose, thereby proving that one oxygen ring in the former is in the same position which it occupies in the remainder of the inulin molecule.

4. Tetra-acetyl-y-fructose obtained as described in 3 above has been condensed with tetra-acetylglucose. In this case also, iso-sucrose octa-acetate was the only crystalline derivative isolated.

5. In none of the condensations now described has any evidence been forthcoming that sucrose derivatives are formed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

PREPARATION OF AMINO-ACETAL

BY JOHANNES S. BUCK AND SAMUEL N. WRENN

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Amino-acetal, $NH_2CH_2CH(OC_2H_5)_2$, on account of its reactivity and versatility, is a synthetic reagent of considerable importance. A search of the literature revealed only three reasonably promising methods, the reduction of nitro-acetal[1] by sodium and alcohol, the reduction of glycine ester by sodium amalgam to amino-acetaldehyde and the conversion of this into amino-acetal,[2] and the action of ammonia on the halogen acetals, which has been investigated by several different workers.[3]

No record was found of attempts to prepare amino-acetal in quantity. For this purpose the action of ammonia on the halogen substituted acetals was investigated. The authors have made use of a steel autoclave of 1100-cc. capacity, fitted with a special ammonia gage and having a working pressure of 1000 pounds. Provision was made for connecting the apparatus to an ammonia tank. With this apparatus a number of runs were made, using chloro-, bromo- and iodo-acetal, and varying the amount of ammonia, the time of heating and the temperature. Chloro- and bromo-acetal proved to be unsatisfactory on account of the low yield and the amount of tarry matter produced; iodo-acetal gave good results.

Experimental

Iodo-acetal was prepared by iodinating acetal in the presence of iodic acid, substantially as described by Hesse[4] and employed by Losanitsch.[5]

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[1] Losanitsch, *Ber.*, 42, 4044 (1909).

[2] Fischer, *ibid.*, 41, 1019 (1908); Neuberg, *ibid.*, 41, 956 (1908).

[3] Natterer, *Monatsh*, 5, 507 (1884); Wohl, *Ber.*, 21, 616 (1888); 39, 1951 (1906); Wolff, *ibid.*, 21, 1481 (1888); Marckwald, *ibid.*, 25, 2354 (1892); Hartung and Adkins, THIS JOURNAL, 49, 2517 (1927).

[4] Hesse, *Ber.*, 30, 1442 (1897).

[5] Losanitsch, *ibid.*, 42, 4044 (1909).

Amino-acetal and **Iodo-acetal.**—In the autoclave were placed 108 g. of iodo-acetal and 600 cc. of alcoholic ammonia, saturated at 0°, and further ammonia was introduced by connecting the autoclave with an ammonia tank for six hours. A pressure of 150 pounds was registered. The cylinder was disconnected and the autoclave heated directly for eleven hours at 110–125°. During the heating period the pressure rose to 375400 pounds and then fell slowly. After allowing the apparatus to cool and releasing any remaining pressure, the reaction mixture was removed, filtered and the alcohol and ammonia distilled off. The residue was taken up in a little water and extracted several times with ether to remove any unchanged iodo-acetal and higher bases. The ether extract thus obtained was dried over solid potassium hydroxide for twelve hours. The aqueous solution was saturated with potassium carbonate and the oil which separated removed. As a precaution the aqueous solution was extracted with ether. The extract was added to the oil and the whole dried over potassium hydroxide for twelve hours, the ether removed and the residue distilled under reduced pressure to remove tar. The distillate was then fractionated at atmospheric pressure, the amino-acetal being collected between 162 and 165°, and the higher-boiling residue worked up as below.

The ether extraction of the reaction mixture, after removal of the ether, was fractionated under reduced pressure, two fractions being obtained (a) up to 125° (10 mm.), (b) 125–140° (10 mm.). The higher fraction, combined with the high-boiling residues from the amino-acetal, gave on refractionation 7 g. of diacetalamine, b. p. 130–138° (10 mm.). The low-boiling fraction was redistilled and the portion boiling at 162–165" (760 mm.) combined with the amino-acetal previously obtained and redistilled several times. In this way 21 g. of amino-acetal, b. p. 162–163°, was obtained.

No unchanged iodo-acetal was found and comparatively little tar was present. The preparation could doubtless be substantially improved by pouring Babbitt metal between the shell and liner of the autoclave and heating the latter in a bath or by steam. Stirring would probably help matters. The temperature of heating should not exceed 125°, as much tar forms above this temperature. The duration of heating should be such that all of the halogen acetal is changed; otherwise general decomposition takes place on distilling the product. As large an excess of ammonia as practicable should be employed, to avoid the formation of secondary and tertiary products.

Amino-acetal from **Chloro-acetal.**—Thirty-five grams of chloro-acetal and 700 cc. of alcoholic ammonia, saturated at 0°, were placed in the autoclave and treated in a manner similar to the previous preparation. The combined yield of amino-acetal, boiling at 160–165°, from four preparations was 12 g. (11.1%).

Amino-acetal from **Bromo-acetal.**—In this preparation 188 g. of bromo-acetal and 400 cc. of saturated alcoholic ammonia were used, and the heating was continued for fourteen hours at 110–115°. From this experiment 24.5 g. of amino-acetal, b. p. 162–166°, and 27 g. of diacetalamine, b. p. 130–140° (8 mm.), were obtained.

Summary

The preparation of amino-acetal is conveniently carried out in a steel autoclave, using iodo-acetal. Iodo-acetal is far superior to chloro- and bromo-acetal and may be readily prepared.

DURHAM, NORTH CAROLINA

[Contribution from the Chemical Laboratory of Northwestern University]

KETENE FROM ACETIC ACID

By Charles D. Hurd and Kenneth E. Martin

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The thermostability of acetic acid was noted many years ago by Cahours[1] and by Berthelot.[2] Nef,[3] however, was the first to study its decomposition in a detailed manner. He reported methane, carbon dioxide, carbon monoxide, ethylene, hydrogen, carbon and acetone as reaction products when the acid vapors were passed over pumice at 500°. Still more recently, these substances and also acetic anhydride were observed by Peytral,[4] who passed acetic acid through an 11-cm. platinum tube at 1150°. She postulated three reactions to explain the results

$$2CH_3CO_2H \longrightarrow H_2O + (CH_3CO)_2O$$
$$CH_3CO_2H \longrightarrow CO_2 + CH_4$$
$$2CH_3CO_2H \longrightarrow 2CH_2O + 2CO + C_2H_4$$

The acetic anhydride reaction has recently been made the subject of patents.[5] The peculiarity of such anhydride formation may not be self-evident. However, almost no other monocarboxylic acid behaves in this manner. Some unusual feature, therefore, must be present in this case.

To provide an interpretation of the mechanism of pyrolysis of acetic acid, the "methane system" has proved useful and interesting. Just as the hydroxyl group serves in the *water system,* or the amino group in the *ammonia system,* so the methyl group is the analog in the *methane system.* On this basis carbonic acid, acetic acid and acetone are structurally similar. The known equations for the decomposition of carbonic acid and of acetone,[6] namely, $HO—CO—OH \longrightarrow H_2O + O{=}C{=}O$, and $CH_3—CO—CH_3 \longrightarrow CH_4 + CH_2{=}C{=}O$, provide a basis for the analogy that acetic acid should break down primarily both into "carbon dioxide + methane" and into "ketene + water." Thus

$$CH_3—CO—OH \longrightarrow H_2O + CH_2{=}C{=}O$$
$$CH_3—CO—OH \longrightarrow CH_4 + O{=}C{=}O$$

In confirmation of this prediction, search for ketene in the reaction products of the acetic acid pyrolysis revealed its presence in appreciable amounts. Ketene unquestionably is the precursor of acetic anhydride, because of its reaction with acetic acid

$$CH_2{=}C{=}O + CH_3CO_2H \longrightarrow (CH_3CO)_2O$$

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[1] Cahours, *Compt. rend.,* 19, 771 (1844); 20, 51 (1845).

[2] Berthelot, *Ann. chim. phys.,* [3] 33, 295 (1851); 53, 187 (1858).

[3] Nef, *Ann.,* 318, 221 (1901).

[4] Peytral, *Bull. soc. chim.,* 31, 113 (1922).

[5] British Patent 194,719, March 10, 1923; U. S. Patent 1,570,514, Jan. 19, 1926; *Chem. Abstracts,* 17, 3509 (1923); 20, 768 (1926) and others.

[6] Hurd, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. IV, p. 39.

Furthermore, it serves to explain the origin of the ethylene and the carbon monoxide: $2CH_2{=}C{=}O \rightarrow C_2H_4 + 2CO$.

Experimental Part

Estimation of **Ketene.**—The following plan was adopted for the determination of the "acetic acid, acetic anhydride, ketene" mixture which was produced by passing acetic acid through a heated tube. The hot effluent vapors were conducted upward through a vertical bulb condenser to remove the bulk of the acid and the acetic anhydride. Remaining traces of these substances were condensed in two ice-cooled U-tubes, which were connected in series at the top of the condenser? From the second U-tube, the gases were conducted into a flask containing an excess of a measured volume of aniline, wherein the available ketene content was quantitatively removed as acetanilide. This value for ketene is certainly lower than the true value because of the fact that some ketene is removed In the condensers either by simple solution or by reaction either with water or with acetic acid.

A series of experiments was carried out to demonstrate that the acetanilide originated largely or entirely from the ketene. In the first place, it was ascertained that acetic acid mixes with aniline with almost no diminution in volume. Thus 9 cc. of aniline and 1.1 cc. of acetic acid gave 10.1 cc. of mixture. Since the increase in volume in the aniline flask was negligible when the ketene vapors (generated from 85 to 600 cc. of glacial acetic acid) were admitted, this is evidence that negligible quantities of acetic acid were introduced. In no case was the increase more than 1 cc. Secondly, it was definitely established by the following tests that acetic acid does not convert aniline in the cold into acetanilide under the conditions of the experiment. (a) One cc. of acetic acid was mixed with an excess of aniline and left for two hours. Then the acid was neutralized with a dilute solution of sodium bicarbonate, extracted with ether, the ether evaporated and the aniline distilled to 200°. There was no trace of residual acetanilide (b) A repetition of (a) with similar results, except that 20 cc. of acid and 20 cc. of aniline were used. (c) Similar to (b) except that 5 g. of acetanilide was purposely admixed at the start. At the conclusion of the experiment 4.8 g of acetanilide was recovered. Finally, since acetanilide may be formed by the interaction of acetic anhydride and aniline in the cold, it was proved that the quantity of acetic anhydride which could have been present was quite insufficient to produce the acetanilide which was isolated. To prove this, the acetic acid and acetic anhydride condensate from Run 4 below was analyzed for the anhydride content by Whifford's method,[8] and was found to contain 0.11 g. of acetic anhydride per cc. of the condensate. Since the total increase in volume of the aniline through which the ketene passed was only one cc., the maximum amount of acetanilide caused by acetic anhydride would be 0.27 g. Presumably even less than this would be formed from this source since acetic anhydride possesses a lower vapor pressure than acetic acid and would tend, therefore, to remain more completely in the condensate. Actually, 4 g of acetanilide was isolated in this run. In Run 6 no acetic anhydride could be detected, yet 3.5 g. of acetanilide was isolated. Its origin must have been from ketene.

Reagents and Apparatus.—Glacial acetic acid was purified by crystallization. The acid was frozen at 15°, filtered off, melted and distilled. The fraction boiling between 115 and 118° was taken. A sample of this fraction melted at 17°. The aniline was also freshly distilled.

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[7] From 600 cc. of original acetic acid in one run at 800°, 480 cc. was recovered by the condenser, 4 cc. by the first U-tube and none by the second.

[8] Whitford, THIS JOURNAL, 47, 2939 (1925).

The apparatus for the pyrolysis was essentially similar to that previously described[9] for the preparation of ketene from acetone. A quartz tube was generally used because of the high temperature required (800°), although similar results were also obtained with a Bohemian glass tube. Porcelain chips were used as packing in both. The temperature was recorded inside the tube by a thermocouple which was sheathed by a small pyrex tube. The quartz reaction tube was heated by the longest unit (16 inches) of an ordinary 3-segmented electric combustion furnace. The acetic acid vapors flowed first through the hot reaction tube, then through a vertical bulb condenser and two ice-cold U-tubes, and finally through a flask which contained 30 cc. of aniline. The remaining gases were inflammable (probably CH_4, CO, C_2H_4) and also contained carbon dioxide (white precipitate with lime water), but they were not otherwise examined.

Pyrolysis.—It was established that little or no decomposition of acetic acid occurred as it was vaporized (by rapid boiling) and passed through a tube at 600° or at 700°. Thus, at 700°, from an original 100 cc. there was almost complete recovery and no trace of acetanilide (*via* ketene) was isolable. At 800°, however, the acid decomposed and ketene was evident in the products. The results of six selected representative experiments are summarized in Table I.

TABLE I

PYROLYSIS OF ACETIC ACID AT 800°

Orig. acetic acid, cc.	Recov. vol., cc.	Acid consumed, cc.	Acrtanilide, g.	Equiv. % yield of ketene
100	80	20	0 6	1.2
100	75	25	0.7	1.2
85	60	25	2	3.4
600	440	160	4	1.1
600	480	120	2.5	0.9
400	280	120	3.5	1.2

The aniline was searched for acetanilide in the following manner. It was washed with a dilute solution of sodium bicarbonate and extracted with ether. Both aniline and ether were distilled off up to 200°, and the residue was dissolved in boiling water, filtered and allowed to cool, These acetanilide crystals were collected on a filter, dried and weighed. In general, the percentage yield of available ketene was 1–2%. Unquestionably, as explained above, the true yield of ketene was greater than this.

Summary

At 800° or higher acetic acid undergoes a reaction of dehydration into ketene as well as a reaction of demethanation into carbon dioxide. These are the primary reactions, but the reactivity of ketene sponsors other effects. Such secondary processes include addition with water or with acetic acid (giving acetic acid and acetic anhydride, respectively) or

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[9] Hurd and Cochran, THIS JOURNAL, 45, 515 (1923); Hurd, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. IV, p. 39.

pyrolysis into carbon monoxide and ethylene. The concept of the "methane system" has been adapted to explain these results.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE PATHOLOGICAL DIVISION, BUREAU OF ANIMAL INDUSTRY]

TREMETOL, THE COMPOUND THAT PRODUCES "TREMBLES" (MILKSICKNESS)

BY JAMES FITTON COUCH

RECEIVED JULY 22, 1929 PUBLISHED DECEMBER 11, 1929

Tremetol is the active principle of two plants, richweed and rayless goldenrod, both of which cause the disease known as trembles. This disease is also known as milksickness, especially by the medical profession. Richweed or white snakeroot (*Eupatorium urticaefolium*) is responsible for the disease in the Central States; rayless goldenrod or jimmy weed (*Aplopappus heterophyllus*,) occurs in the Southwestern section of the United States, where it produces the same disease.

Extensive pharmacological study, the results of which have been published in other places[1] has demonstrated that the active constituent of these plants is a substance to which the name tremetol has been applied. This paper contains the results of the chemical study of tremetol.

To prepare tremetol the following procedure has been used successfully. The plant material should be fresh in the case of richweed; rayless goldenrod is still poisonous when dried but appears gradually to lose toxicity. Old dried richweed does not produce trembles. The plant is comminuted and extracted with alcohol. The solvent is distilled from the extract, best under diminished pressure, and the greenish fatty residue is extracted with boiling water as long as anything dissolves. The insoluble material is collected and thoroughly extracted with boiling 50% alcohol. The solvent is removed from this solution and the thick resinous mass that separates is allowed to cool and harden, when the watery portion of the residue may be poured off it. The resinous mass is now thoroughly extracted with boiling 30% alcohol and the solution is filtered hot from the insoluble matter. On cooling the filtrate crude tremetol ester separates. A further crop may be obtained by evaporating the alcohol from the mother liquors. The combined crops are now hydrolyzed by boiling with 5% alcoholic potash for four hours, the alcohol is distilled off and the residue is dissolved in water. The free tremetol is extracted from this solution with successive portions of ether. The ether solutions are united, concentrated to convenient volume and washed, first with dilute sodium hydroxide solution and then with water, to remove possible phenols and resin acids. The purified ether solution is now mixed with 4 volumes of petroleum ether, filtered from any precipitate and allowed to evaporate. The solution in ether and reprecipitation with petroleum ether should be repeated twice to insure purity. On removal of the solvent tremetol remains as a straw-yellow, thick oil of pleasant aromatic odor distantly reminiscent of clove and nutmeg. Should solid, waxy particles separate, the substance has not been thoroughly separated from a sterol that accompanies it in richweed

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[1] *J. Agric. Res.*, *35*, 547–576 (1927); *J. Am. Med. Assocn.*, *91*, 234–6 (1928); *J. Am. Vet. Med. Assocn.*, (n. s.) *26*, 603–605 (1928). A report on rayless goldenrod is in course of publication.

and the 50 and 30% alcohol steps should be repeated. Criteria of purity are the optical rotation, index of refraction and molecular weight.

Properties of Tremetol.—Tremetol is a straw-yellow thick oil of aromatic odor. It has not been obtained in crystalline condition and decomposes when attempts to distil it are made, even when the pressure is reduced to 3 mm. It is slowly volatile in steam and appears to suffer some alteration during the process. Tremetol is insoluble in water, acids and alkalies. It is readily soluble in alcohol and the common organic solvents, less soluble in petroleum ether but readily in mixtures of that solvent with ether. It occurs in the plant in combination with a resin acid the chemical composition of which has not been determined. Tremetol readily oxidizes in the air, losing its characteristic odor and developing a rancid and acetous odor.

The analytical figures for tremetol indicate either of two formulas, $C_{16}H_{22}O_3$ or $C_{17}H_{24}O_3$, agreeing better with the latter. Molecular weight determinations, bromine absorption and molecular refractivity data agree closely with the requirements of the first formula and this has been chosen as the more likely. The high percentages of carbon and hydrogen found by analysis are considered to be due to small amounts of petroleum ether remaining in the tremetol, which cannot be driven off without decomposing the substance itself.

Tremetol absorbs four atoms of bromine per molecule at room temperature. Inasmuch as the formula indicates the presence of five double bonds, it may be concluded that the substance contains a phenyl nucleus and a side chain containing two double bonds. The function of the oxygen atoms has not been determined. Phenolic hydroxyls and alkoxyl groups are not detected by the appropriate tests. No crystalline oxime or hydrazone has been obtained. Aldehyde and carboxyl groups are absent. A study of the constitution of the substance is in progress.

Anal. Calcd. for $C_{16}H_{22}O_3$ (262.17): C, 73.24; H, 8.45. Calcd. for $C_{17}H_{24}O_3$ (274.18): C, 73.87; H, 8.75. Found: (substance from richweed) C, 73.89, 73.89, 73.33; H, 8.89, 8.58, 8.60; mol. wt., 257, 259; (substance from rayless goldenrod) C, 73.54, 73.72, 73.57; H, 8.66, 8.83, 8.94; mol. wt., 237, 262, 258. ***Optical activity.*** 2.9020 g. in enough alcohol to make 100 cc. rotated the plane of polarized light an average of 0.98° to the left when examined in a 10-cm. tube at 30°: whence $[\alpha]^{30}_{D}$ $-33.82°$.

Bromine Absorption.—In carbon tetrachloride solution 0.3882 and 0.4359 g. of the substance absorbed 0.4531 and 0.5466 g. of bromine at room temperature, or 1.167 and 1.254 g. of bromine per gram of substance (mol. wt. 262.17). One molecule of substance **with two** active double bonds reacting with four atoms of bromine requires 1.22 g. of halogen per gram; d^{25}_{4} 1.0787, n^{30}_{D} 1.5345, mol. refr. calcd. for $C_{16}H_{22}O_3$ (F_5), 76.12; for $C_{17}H_{24}O_5$ (F_5), 79.65. Found: 75.62.

Summary

Tremetol, the substance present in richweed and in rayless goldenrod, which produces the diseases known as milksickness and trembles is a straw yellow oil, $C_{16}H_{22}O_3$, levorotatory, insoluble in water, acid and alkaline solutions, and soluble in the common organic solvents.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXI. BETA-THIOPHENOL GLYCOSIDES OF GLUCOSE, XYLOSE, LACTOSE AND CELLOBIOSE[1,2]

BY CLIFFORD B. PURVES

RECEIVED JULY 22, 1029 PUBLISHED DECEMBER 11, 1929

Although the glycosides of the hydroxy alcohols form a numerous group which has been submitted to detailed study and whose optical properties have been classified through the work of Hudson,[3] too few of the thioglycosides have been prepared to render possible a similar mathematical examination of their molecular rotations. Apart from the *a*- and β-glucosides of methyl, ethyl, propyl and benzyl mercaptan described by Schneider and his co-workers,[4] the only other simple members of the series found recorded in the literature are β-thiophenol glucoside and β-thiophenol lactoside, which together form the subject of a paper by Fischer and Delbrück.[5] The thioglycosides, nevertheless, are of interest from an optical point of view, for they differ from their oxygen analogs in containing a bivalent and therefore unsaturated sulfur atom directly united to the first asymmetric center of the carbohydrate residue. It is impossible to predict the nature and the extent of the changes which this difference may bring about in their behavior toward plane-polarized light and, in consequence, the present investigation is one of several designed to gain information on this subject by experimental methods. This article is mainly concerned with four glycosides of thiophenol and with their acetylated derivatives.

At an early stage in the research it became apparent that an acetobromo sugar in ethereal or benzene solution reacted very slowly and sometimes incompletely with sodium thiophenate dissolved in water. This was the

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[1] Publication approved by the Director of the Bureau of Standards, U. S. Department of Commerce.

[2] The author has arranged with Dr. C. S. Hudson, under whose direction the research was carried out, that it will be included as No. XXI in his series entitled "Relations between Rotatory Power and Structure in the Sugar Group." No. XX was published in THIS JOURNAL, 51,2788 (1929).

[3] Hudson, *ibid.*, 31, 66 (1909).

[4] Schneider, Sepp and Stiehler, Ber., 51, 220 (1918).

[5] Fischer and Delbrück, *ibid.*, 42, 1476 (1909).

method used by Fischer and Delbrück[5] for preparing the acetylated derivatives of thiophenol glucoside and lactoside, but its tedious nature and somewhat uncertain outcome led to its abandonment in the present work. The acetobromo sugars studied, however, swiftly condensed with potassium thiophenate when means were taken to render the system homogeneous, and the yield of the acetylated thioglycosides was satisfactory when the alkalinity of the solution was low. These conditions were readily obtained by adding the acetobromo sugar, dissolved in chloroform, to an equal bulk of 95% alcohol containing one equivalent of potassium hydroxide and a 10 to 15% excess of the mercaptan, an excess which was sufficient to render the alcoholic solution neutral to litmus and to phenolphthalein. After the reaction had been completed by heating, the clear liquor was washed free of potassium bromide, alcohol and thiophenol by very dilute aqueous sodium bicarbonate and the product was recovered in an almost pure condition from the chloroform residue. It will be seen that this procedure was very similar to that adopted by Schneider, Sepp and Stiehler[4] but differs from it in that a reacetylation of the glycoside was unnecessary. This was due to the strongly acidic nature of thiophenol and to the particular excess of the reagent which was used. Moreover, the acetobromo derivative was prepared from the fully acetylated sugar by the action of hydrogen bromide dissolved in a mixture of glacial acetic acid and chloroform. After the substitution of bromine for acetyl was complete, washing with water removed the free acids and the residual chloroform, containing almost the theoretical amount of the acetobromo sugar, was run into the solution of alcoholic potassium thiophenate without previous drying. This simplification rendered it possible to obtain a 70% yield of the β-thiophenol glycoside acetate from the crude, fully acetylated sugar in the course of six hours.

Five new compounds are described in the experimental portions: the β-thiophenol and the β-*p*-thiocresol glycosides of cellobiose together with the acetate of the former; β-thiophenol xyloside triacetate and β-thiophenol xyloside itself. In addition, it was necessary to repeat the work of Fischer and Delbruck on the thiophenol derivatives of glucose and lactose, partly to confirm and to extend the optical data which they record for these substances and partly to make sure that the new method gave products identical with those formerly described. All of the thioglycosides examined were crystalline and a summary of their physical properties will be found below.

A simple way of analyzing the molecular rotations of the fully acetylated thioglycosides is to adopt the method used by Hudson[6] to calculate the rotation, A_{Cl}, of the potentially reducing asymmetric carbon atom of the acetochloro sugars. Assuming, as a first approximation, that substitution

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[6] Hudson, This Journal, 46, 462 (1924).

in this position does not affect the optical rotatory power of the other asymmetric centers in the molecule, the combined molecular rotation in chloroform of the latter may be denoted by B. The values of B for the various acetylated sugar residues were obtained by the above author from his study of the α- and @-acetates themselves and are listed in the table below. Then if A_{SPh} be the molecular rotation due to the asymmetric carbon atom to which the thiophenyl radical is attached, $B-A_{\mathrm{SPh}}$ is the observed molecular rotation of the β-thiophenol glycoside acetate and the magnitude of A_{SPh} may be calculated in each case. These values, together with those quoted from the work of Hudson for A_{Cl}, the sum A_{SPh} plus A_{Cl} and the difference, A_{SPh} minus A_{Cl}, are also given.

TABLE I

COMPARISON OF THE QUANTITIES A_{SPh} AND A_{Cl}, THE MOLECULAR ROTATIONS, RESPECTIVELY D# TO THE TERMINAL ASYMMETRIC ATOM IN THE β-THIOPHENOL GLYCOSIDE ACETATES AND IN THE ACETOCHLORO DERIVATIVES Ob THE SUGARS

Sugar	$B-A_{\mathrm{SPh}}$	B	A_{SPh}	A_{Cl}	$A_{\mathrm{Cl}}-A_{\mathrm{SPh}}$	$A_{\mathrm{Cl}}+A_{\mathrm{SPh}}$
Xylose	−21,670	10,200	−31,870	38,500	70,370	6,630
Cellobiose	−20,740	8,800	−29,540	39,000	68,540	9,460
Lactose	−14,270	16,900	−31,170	38,100[7]	69,270	6,930
Glucose	− 7,700	20,700	−28,400	40,200	68,600	11,800
		Mean value M_D	−30,500	38,950	69,200 in $CHCl_3$	

Inspection of the data shows that A_{SPh}, like A_{Cl}, is an almost constant quantity and that the greatest deviation from the mean value occurs with tetra-acetyl thiophenol glucoside. This error corresponds to less than 5° in specific rotation and the agreement may be considered fair. Thiophenol glycoside acetates, therefore, obey the regularities discovered by Hudson for other similar series of sugar derivatives and the possession of an unsaturated sulfur atom does not necessarily render invalid the principle of optical superposition on which such regularities are founded. It is worthy of note that the molecular rotation of the p-thiocresyl group, M_D *29,580* as obtained from that of hepta-acetyl β-*p*-thiocresol cellobioside, M_D *−20,780* in chloroform, is practically the same as that of A_{SPh}, as might have been expected from the close structural similarity between these two radicals.

While it is true that A_{SPh} is approximately constant, the deviations from the average value would individually be zero if the law of optical superposition were obeyed with rigor. This is obviously not the case and different substituents occasion varying small but definite changes in the rotation of the rest of the molecule. The remarkable constancy of the sum $A_{\mathrm{Cl}}+A_{\mathrm{SPh}}$, as compared with the gross variations in their difference, $A_{\mathrm{Cl}}-A_{\mathrm{SPh}}$, indicates that in the former case the secondary

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[7] Hudson and Kunz, THIS JOURNAL, 47,2052 (1925).

deviations were largely compensated and were, therefore, very similar in magnitude and opposite in sign. As the thiophenyl glycoside acetates, from their method of preparation, possessed the β-configuration and were therefore contrary in this respect to the acetochloro sugars, it may be concluded that the thiophenyl group very closely resembles a chlorine atom in its effect upon the rotation of an acetylated sugar molecule as a whole. Indeed, an exhaustive series of similar calculations showed that this parallelism between thiophenyl, p-thiocresyl and chlorine substituents in the reducing position of the four sugar acetates studied was as close as that between chlorine and iodine in the acetohalogen derivatives, much better than that between chlorine and bromine, chlorine and α-methoxy or β-thiophenyl and β-methoxyl. In a word, the molecular rotations of the thiophenol glycoside acetates in chloroform are appropriately compared with those of the acetochloro derivatives and not with the acetylated glycosides of the hydroxy alcohols.

While the acetylated thiophenol glycosides display the normal relationship to each other in their optical behavior, no such claim can be made for the β-glycosides themselves. The following data are based throughout upon measurements made in water, while a_{SPh} and b have their old significance but with respect to the new solvent. An article by Hudson[8] furnished the data from which the value of b was calculated from the molecular rotations of the β-sugars in the usual way. It will be seen that the variation in the magnitude of a_{SPh} is very great.

TABLE II

VALUE OF THE QUANTITY, a_{SPh}, THE ROTATION OF THE END ASYMMETRIC CARBON ATOM FOR β-THIOPHENOL GLYCOSIDES

Sugar	M_D in water $b - a_{SPh}$	M_D b	M_D a_{SPh}
Xylose	−17,130	7,250	24,380
Cellobiose	−25,690	13,970	39,660
Lactose	−17,060	20,470	37,530
Glucose	−19,180	11,870	31,050

If the very probable assumption be made that the deacetylation of the acetylated thioglycosides by means of alcoholic ammonia was accompanied by no other structural change in the molecule, only two explanations seem to be able to account for the inconstancy of a_{SPh}. The first of these would postulate that the unsaturated sulfur atom in the thioglycoside formed an unstable addition compound with an hydroxy group in the carbohydrate residue or with the elements of the water used as a solvent in the optical determinations. In this case the experimental observations could be attributed to the constitutional dissimilarity of the compounds studied. On the other hand, the anomalies may be due to the failure of

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[8] Hudson, THIS JOURNAL, 47, 268 (1925).

the principle of optical superposition to apply even approximately to **the** glycosides of thiophenol, but it then becomes difficult to understand why the same irregularities are not more marked among the rotations of the fully acetylated derivatives. **The** exploration of this possibility would involve the study of reducing sugars substituted in the first position by other highly acidic radicals such as chlorine in the unknown chloro sugars. In the meantime, however, it is unsafe to make use of an optical property as a guide to the stereochemical arrangement of the unsubstituted thioglycosides.

Experimental

The Preparation of **Triacetyl β-Thiophenol Xyloside.**—A solution of 10 g. of pure β-xylose tetra-acetate in 25 cc. of dry chloroform was made up to 50 cc. with glacial acetic acid saturated with hydrogen bromide. The optical rotation of the mixture increased to a constant value within thirty minutes, when the substitution of bromine for the acetyl group on the first carbon atom of the molecule was taken to be complete. After three successive washings with ice water had removed acetic acid and hydrogen bromide, the residual chloroform solution of acetobromoxylose, together with small chloroform extracts of the aqueous liquors, was added at room temperature and without drying to the equivalent amount (51 cc.) of 0.612 *N* alcoholic caustic potash in which 3.5 cc. or a 10% excess of thiophenol had previously been dissolved. Warming on the water-bath for thirty minutes rendered the condensation complete, after which the clear liquor, with its deposit of crystalline potassium bromide, was repeatedly washed in a separatory funnel with a dilute aqueous solution of sodium bicarbonate until the odor of the thio-alcohol became faint. The chloroform layer, after being finally extracted with water and dried over anhydrous calcium chloride, was evaporated under diminished pressure to a thin sirup, from which an 80% yield of triacetyl-β-thiophenol xyloside was precipitated by the cautious use of light petroleum. The product, which occurred as small, well-formed prisms, was readily recrystallized by adding petroleum ether to its ethereal solution and after two such purifications possessed a specific rotation in chloroform of $[\alpha]_D$ −58.71° (0.2566 g. in 25 cc. rotated plane-polarized light 1.205° to the left when a 2-dm. tube was used). Another recrystallization failing to change this value appreciably (found, $[\alpha]^{20}_D$ −59.0"; 0.3758 g. in 25 cc. of chloroform gave an observed reading of 1.774" to the left when in a 2-dm. tube), the specific rotation of pure triacetyl-β-thiophenol xyloside in chloroform was accepted as $[\alpha]^{20}_D$ −68.9'. The compound was readily soluble in all of the usual organic solvents save petroleum ether and melted sharply at 78°.

An acetyl determination was carried out by the method of Kunz;[9] 0.3174 g. required 26.13 cc. of decinormal alkali in place of the theoretical amount, 25.88 cc., for triacetyl thiophenol xyloside. In the estimation of sulfur the accurate and expeditious method due to Waters[10] was adopted: 0.3566 g. gave 0.2346 g. of Ba_2SO_4. Calcd.: S, 8.70. Found: S, 9.02.

Hepta-acetyl-β-thiophenol Cellobioside.—Pure β-cellobiose octa-acetate, 30 g., was allowed to stand for three hours at room temperature in chloroform (90 cc.) and glacial acetic acid containing 20% by weight of hydrogen bromide (75 cc.). Occasional shaking had enabled the acetate to dissolve completely and a solution of the acetobromo sugar in chloroform was isolated from the mixture as described in the preceding pare-

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[9] Kunz and Hudson, THIS JOURNAL, 48, 1982 (1926).

[10] Waters, *J. Ind. Eng. Chem.*, 12,482 (1920).

graph. The condensation of the acetobromocellobiose with the theoretical amount (96 cc.) of 0.455 *N* alcoholic caustic potash and with 4.8 cc. (10% excess) of thiophenol was also carried out exactly as in the case of triacetyl thiophenol xyloside and, on isolation, a 78% yield of crude crystalline acetylated thioglycoside was obtained. A single recrystallization from 16 times its weight of hot alcohol lowered the specific rotation of the preparation to $[\alpha]^{20}_{\mathrm{D}}$ —26.57' in chloroform but this method did not succeed in eliminating all of the impurities. The crude material, which contained no halogen and displayed little reducing power on hot Fehling's solution, was eventually dissolved in 100 cc. of warm chloroform and was fractionally recrystallized as minute needles by the cautious addition of hot absolute alcohol. This procedure gave a small first fraction with a specific rotation of $[\alpha]^{16}_{\mathrm{D}}$ —27.2" in chloroform (0.2485 g. in 25 cc. had a —0.541° in a 2-dm. observation tube) and a large second fraction with $[\alpha]^{16}_{\mathrm{D}}$ —28.5° (0.4633 g. in 25 cc. of chloroform gave an observed reading of 1.056° to the left in a 2-dm. tube). The specific rotation of the latter fraction did not change appreciably on repeated purification in the same manner; after the first recrystallization, $[\alpha]^{17}_{\mathrm{D}}$ —28.33° (0.5428 g. in 25 cc. of chloroform had a —1.230° in a 2-dm. tube); after the fourth, $[\alpha]^{18}_{\mathrm{D}}$ —28.58" (0.5421 g. gave an observed reading of 1.230° to the left); and after the fifth, $[\alpha]^{20}_{\mathrm{D}}$ —28.20° (0.5343 g. had a —1.205" observed in 25 cc. of chloroform with a 2-dm. tube). Accordingly, $[\alpha]^{20}_{\mathrm{D}}$ —28.5° was accepted as the true specific rotation of hepta-acetyl-β-thiophenol cellobioside in chloroform. The compound decomposed in the neighborhood of 295° and dissolved freely in chloroform and acetone, was sparingly soluble in hot alcohol and was almost insoluble in ether or petroleum ether.

In an acetyl estimation, 0.2287 g. required 21.8 cc. of decinormal alkali, the amount calculated for the same weight of thiophenol cellobioside acetate being 22.0 cc. The preparation contained 4.57% of sulfur in place of the theoretical amount, 4.40% (0.5349 g. gave 0.1785 g. of $BaSO_4$).

Hepta-acetyl-β-*p*-thiocresol Cellobioside.—The method used to obtain hepta-acetyl-β-thiophenol cellobioside was also adopted in the preparation of the analogous p-thiocresol derivative and gave rise to the product as long, silky needles in a yield which was 80% of the theoretical. The specific rotation of the crude product was $[\alpha]^{21}_{\mathrm{D}}$ —22.8' in chloroform (0.3323 g. in 25 cc. had a —0.606" in a 2-dm. tube) but two recrystallizations from alcohol reduced this figure to $[\alpha]^{20}_{\mathrm{D}}$ —28.2° (0.3438 g. gave an observed reading of 0.776° to the left). No change occurred after the next purification (found, $[\alpha]^{20}_{\mathrm{D}}$ —27.75°; 0.3385 g. in 25 cc. of chloroform gave an observed reading of 0.751° to the left) and $[\alpha]^{20}_{\mathrm{D}}$ —28.0° was taken to be the correct rotation of hepta-acetyl-β-*p*-thiocresol cellobioside in this solvent. The substance melted sharply at 217°.

In an acetyl estimation 0.2726 g. required 25.04 cc. of decinormal alkali, the theoretical amount being 25.15 cc.; 0.4923 g. also gave 0.1529 g. of $BaSO_4$. Found: S, 4.26; hepta-acetyl thiocresol cellobioside requires, S, 4.31.

Hepta-acetyl-β-thiophenol Lactoside.—The acetylated thioglycoside was prepared from 40 g. of crude lactose octa-acetate, free from inorganic salts but not recrystallized, exactly as in the case of the same derivative of cellobiose, and the yield of the crude crystalline product averaged 70% of the theoretical. Recrystallization from 130 cc. of hot 95% alcohol reduced the specific rotation to $[\alpha]^{20}_{\mathrm{D}}$ —19.25' (0.3552 g. had a reading of 0.547' to the left in 25 cc. of chloroform and a 2-dm. tube), while after the next purification a value of $[\alpha]^{20}_{\mathrm{D}}$ —19.6" was observed (0.2916 g. in 25 cc. with a 2-dm. tube gave 0.457' to the left). The product from the third recrystallization had $[\alpha]^{20}_{\mathrm{D}}$ —19.72° (0.3270 g. gave a reading of —0.516") and $[\alpha]^{20}_{\mathrm{D}}$ —19.6" was the specific rotation of pure hepta-acetyl-β-thiophenol lactoside in chloroform solution at a concentration of about 1.5%.

Fischer and Delbrück[5] quote $[\alpha]^{20}_{\mathrm{D}}$ —17.7° as the specific rotation of the substance in a 7.165% chloroform solution; the present preparation gave an observed reading of 2.599' to the left in a 2-dm. tube under the same conditions and therefore possessed a specific rotation of $[\alpha]^{20}_{\mathrm{D}}$ −18.14° at this concentration. The compound melted at 155–156°.

In an acetyl estimation, 0.1652 g. required 15.88 *cc.* of decinormal alkali while the value demanded by the same weight of acetylated thiophenol lactoside is 15.85 cc. The sulfur estimation on 0.4831 g. gave 0.1567 g. of $BaSO_4$. Found: S, 4.46; calcd., S, 4.40.

Tetra-acetyl-β-thiophenol Glucoside.—The substance was prepared by the above method in 70% yield from crude crystalline glucose penta-acetate and was recrystallized from 95% alcohol as long needles with a specific rotation of $[\alpha]^{20}_{\mathrm{D}}$ −22.25' in chloroform (0.1653 g. in 25 cc. had an observed reading of 0.294° to the left in a 2-dm. tube). Two fractions were obtained in the third recrystallization with rotations of $[\alpha]^{19}_{\mathrm{D}}$ −17.5" and $[\alpha]^{20}_{\mathrm{D}}$ −17.38°, respectively (0.6482 g. had a −0.907"; 0.6786 g. had α −0.943" under the usual conditions) and the next recrystallization did not change the determination (found, $[\alpha]^{20}_{\mathrm{D}}$ −17.63°; 0.6745 *g.* had α −0.951"). Pure tetra-acetyl-β-thiophenol glucoside, therefore, had a specific rotation in chloroform of $[\alpha]^{20}_{\mathrm{D}}$ −17.8" for a concentration of about 2.5%.

Fischer and Delbriick[5] made an observation in toluene of $[\alpha]^{20}_{\mathrm{D}}$ −40.1° for a concentration of 4.6784%; two determinations in this solvent, carried out under comparable conditions, gave values of $[\alpha]^{21}_{\mathrm{D}}$ −40.85" and $[\alpha]^{21}_{\mathrm{D}}$ −40.7° for the specific rotation, or a mean value of $[\alpha]^{21}_{\mathrm{D}}$ −40.8°, in good agreement with the earlier observations (0.1696 *g.* in 25 cc. of toluene had α −3.828"; 1.1410 g. in 25 cc. had α −3.699").

β-Thiophenol Xyloside.—Pure triacetyl-β-thiophenol xyloside was dissolved in six times its weight of methyl alcohol which had previously been saturated at room temperature with dry ammonia gas. After standing overnight the evaporation of the solvent left a sirup which was repeatedly extracted with warm dry ether to remove acetamide. The product then crystallized in almost quantitative yield as stout prisms with a specific rotation in water of $[\alpha]^{20}_{\mathrm{D}}$ −69.7° after a single purification from alcohol (0.2905 g. in 25 cc. gave a reading of 1.621° to the left in a 2-dm. tube). A second recrystallization gave a product with $[\alpha]_{\mathrm{D}}$ −71.0" (0.2748 g. had α −1.562") which was not changed by the third or by the fourth (found, $[\alpha]^{20}_{\mathrm{D}}$ −70.5" and $[\alpha]^{20}_{\mathrm{D}}$ −71.0"; 0.2933 g. gave a reading of 1.654°, 0.3420 g. one of 1.943" to the left in a 2-dm. tube when dissolved in 25 cc. of water). β-Thiophenol xyloside thus possessed a specific rotation of $[\alpha]^{20}_{\mathrm{D}}$ −70.8° in a 1.4% aqueous solution. In acetone the optical property was very different (0.1581 g. in 25 cc. of the pure solvent gave an observed reading of 1.101" to the left in a 2-dm. tube and $[\alpha]^{20}_{\mathrm{D}}$ was −87.05"). The compound melted sharply at 144° and in addition to a ready solubility in water and alcohol it dissolved freely in acetone and ethyl acetate.

In an estimation of sulfur, 0.1951 g. gave 0.1894 g. of $BaSO_4$. Found: S, 13.33; calcd. for thiophenol xyloside, S, 13.23.

β-Thiophenol Cellobioside.—After the deacetylation of the pure hepta-acetate with methyl alcoholic ammonia and the removal of acetamide with ether, the addition of a little alcohol caused the glycoside to crystallize in a yield of 67% of the theoretical. The minute crystals separated over the course of days from methyl alcohol containing a little ether and possessed a rotation of $[\alpha]^{16}_{\mathrm{D}}$ −54.7 in water (0.2584 g. in 25 cc. had α −1.131"). Two similar recrystallizations raised this value to $[\alpha]^{16}_{\mathrm{D}}$ −59.0° (0.3836 g. gave a reading of α −1.811°), which was not changed by further purification (found $[\alpha]^{17}_{\mathrm{D}}$ −59.3'; 0.4020 had α −1.907'). β-Thiophenol cellobioside, therefore, had a specific rotation of $[\alpha]^{17}_{\mathrm{D}}$ −59.2° in water for a 1.5% solution. The melting point was sharp at 230°.

The sulfur estimation, carried out on 0.3696 g., gave 0.2029 g. of $BaSO_4$. **Found:** S, 7.54; calcd., S, 7.37.

β-Thiophenol Lactoside.—By the deacetylation of the pure acetate, crystalline thiophenol lactoside was obtained in 80% of the theoretical yield. Two recrystallizations from 95% alcohol rendered the compound nearly pure (found, $[\alpha]^{19}_{D}$ −38.45°; 0.2477 g. in 25 cc. of water had α −0.762"). After the third, the specific rotation was $[\alpha]^{19}_{D}$ −39.45" (0.2436 g. rotated plane-polarized light 0.786' to the left under the usual conditions), while no significant change was observed after the fourth purification (found, $[\alpha]^{19}_{D}$ −39.13"; 0.2345 g. in 25 cc. of water had **a** −0.734' when observed in a 2-dm. tube). The specific rotation of pure β-thiophenol lactoside in about 1% aqueous solution was thus $[\alpha]^{19}_{D}$ −39.3°. At a higher concentration, 6.5632%, the rotation of this glycoside was $[\alpha]^{19}_{D}$ −40.36" (1.6408 g. in 25 cc. of water gave a reading of 5.296" to the left in a 2-dm. tube), in good agreement with the value, $[\alpha]^{20}_{D}$ −40.1 °, obtained by Fischer and Delbrück[5] under the same conditions. β-Thiophenol lactoside melted sharply at 220°.

In a sulfur estimation, 0.5004 g. gave 0.2651 g. of $BaSO_4$. Found: S, 7.28; calcd. for thiophenol lactoside, S, 7.37.

β-Thiophenol Glucoside.—The sirupy mixture of acetamide and thioglucoside which remained from the deacetylation of pure tetra-acetyl-p-thiophenol glucoside was dissolved in 7 times its weight of warm ethyl acetate and 86% of the theoretical amount of thiophenol glucoside crystallized as the solution cooled. After two further recrystallizations from ethyl acetate containing a little methyl alcohol, the product had a rotation of $[\alpha]^{20}_{D}$ −70.34° in water (0.5352 g. in 25 cc. had an observed rotation of 3.012" to the left in a 2-dm. tube) and melted sharply at 133°. These values were not changed on further purification (found, $[\alpha]^{19}_{D}$ −70.75"; 0.5323 g. had **a** −3.012°) and the specific rotation of β-thiophenol glucoside in a 2% aqueous solution was regarded as $[\alpha]^{19}_{D}$ −70.5". When the concentration was 9.774%, the rotation fell to $[\alpha]^{19}_{D}$ −72.15' (observed in a 2-dm. tube, 14.76° to the left) in good agreement with the values of $[\alpha]_D$ −72.3" and $[\alpha]_D$ −72.5" found by Fischer and Delbrück for the same solution.

The author desires to thank the Commonwealth Fund of New York for the Fellowship which made possible the carrying out of this research. He also expresses his deep indebtedness to Dr. C. S. Hudson for many valuable suggestions.

Summary

1. The specific rotations of the following thioglycoside acetates have been measured in chloroform solution: triacetyl-β-thiophenol xyloside, m. p. 78°, $[\alpha]^{20}_{D}$ −58.9°; hepta-acetyl-β-thiophenol cellobioside, decomposition point about 295°, $[\alpha]^{20}_{D}$ −28.5°; hepta-acetyl-β-*p*-thiocresol cellobioside, m. p. 217', $[\alpha]^{20}_{D}$ −28.0'; hepta-acetyl-β-thiophenol lactoside, m. p. 155–156°, $[\alpha]^{20}_{D}$ −19.6°; tetra-acetyl-p-thiophenol glucoside, m. p. 117°, $[\alpha]^{20}_{D}$ −17.5°.

2. It has been shown that the molecular rotation of the potentially reducing carbon atom in the above acetylated thioglycosides, A_{SPh}, is approximately constant at M_D 30,500. The deviations from this value in the case of individual sugars are similar in magnitude but opposite in sign to those of A_{Cl}, the molecular rotation of the terminal asymmetric atom of the acetochloro derivatives.

3. The following specific rotations were measured with precision in aqueous solution; β-thiophenol xyloside, m. p. 144°, $[d]_D^{20}$ −70.8°; β-thiophenol cellobioside, m. p. 230°, $[\alpha]_D^{17}$ −59.2°; β-thiophenol lactoside, m. p. 220°, $[\alpha]_D^{19}$ −39.3" and β-thiophenol glucoside, m. p. 133°, $[\alpha]_D^{19}$ −70.5°.

4. The molecular rotations in water of the above four β-thiophenol glycosides displayed irregularities which could not be explained. In consequence, optical data cannot at present be safely used as an aid in determining the stereochemical configuration of the thioglycosides.

WASHINGTON, D. C.

[CONTRIBUTION PROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXII. EVIDENCE CONCERNING THE RINGED STRUCTURE OF BETA-THIOPHENOL CELLOBIOSIDE AND OF BETA-THIOPHENOL LACTOSIDE[1,2]

BY CLIFFORD B. PURVES

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A noteworthy property of the β-thioglycosides which serves to distinguish them from the isomeric a-forms, and also from the glycosides of the hydroxy alcohols, may be seen in their great stability toward acid hydrolysis.[3] The glycosidic unions in β-thiophenol lactoside and cellobioside are no exceptions to the general rule and the comparative indifference of the thio linking in such derivatives of the disaccharides makes possible a simple way of examining their constitution. For example, if thiophenol lactoside be submitted to the action of aqueous acid under conditions just sufficiently drastic for the complete hydrolysis of the disaccharide itself, the union of thiophenol with the potentially reducing carbon atom of the sugar residue is largely preserved and galactose and a thiophenol glucoside may be expected to form the main products of the reaction. The former component may readily be modified before its examination, either as regards the position of the oxygen ring or otherwise, and the isolation of galactose of the ordinary type therefore provides no evidence concerning its original state in the disaccharide molecule. It is otherwise

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[1] Published by permission of the Director of the Bureau of Standards, U. S. Department of Commerce.

[2] The author has arranged with Dr. C. S. Hudson, under whose direction the research was carried out, that it will be included as No. XXII in his series entitled "Relations between Rotatory Power and Structure in the Sugar Group." No. XXI was published in THIS JOURNAL, 51,3619 (1929).

[3] Schneider, Sepp and Stiehler, *Ber.*, 51,220 (1918).

with the thioglycosidic component, for here the reducing position is shielded by the stable thiophenol radical and a change in the structure of this unit of thiophenol lactoside during the experiment may be discounted with some confidence. Thiophenol lactoside and cellobioside have accordingly been submitted to the action of aqueous acid and the specimens of thiophenol glucoside so obtained have been examined in order to see whether they were of the normal or gamma type.

After making certain that thiophenol glucoside itself was very nearly stable under the experimental conditions to be employed in the hydrolyses, thiophenol lactoside was heated with normal sulfuric acid for one and three-fourths hours. The trace of thiophenol set free during this operation was readily removed by chloroform and it was possible to determine the final specific rotation of the solution to be $[\alpha]_D$ −10.66". An equimolecular mixture of galactose and β-thiophenol glucoside possesses the closely similar rotation of $[\alpha]_D$ −9.56" in distilled water. Ethyl acetate separated the non-reducing product from the crystalline galactose, which was also identified, and the extract was found to contain 75.4% of the theoretical amount of β-thiophenol glucoside in one experiment and 84% in a second. The physical constants of the product, m. p. 125–128°, $[\alpha]_D$ −65.9° in water, although improved by subsequent recrystallization, could not be made to agree with those of pure β-thiophenol glucoside, m. p. 133°, and $[\alpha]_D$ −70.5" and the impure specimen was acetylated. A tetra-acetyl-β-thiophenol glucoside was thus obtained in 90% yield which possessed the same crystalline form, melting point and specific rotation as a standard preparation from glucose itself. Fischer and Delbrück[4] also carried out this hydrolysis with a similar result but unfortunately the scale of their experiment was too small to permit of the rigorous characterization of the particular type of thioglucoside which had been formed. It was therefore necessary to repeat their work.

The partial hydrolysis of β-thiophenol cellobioside was carried out in precisely similar fashion and yielded glucose, identified as glucosazone, and slightly impure β-thiophenol glucoside of the ordinary variety, identified as such and also as the pure tetra-acetate, m. p. 117°, $[\alpha]_D$ −17.84" in chloroform. Although the hydrolysis of the thiocellobioside was discontinued when the specific rotation of the solution had increased to $[\alpha]_D$ −23.0°, that is, in close agreement with that of an equimolecular mixture of glucose and β-thiophenol glucoside, $[\alpha]_D$ −21.5" in water, the yield of thiophenol glucoside extracted by ethyl acetate was only 51% of the theoretical. The easy separation of amorphous galactose from thiophenol glucoside by the same solvent stands in contrast to this observation.

From the foregoing, thiophenol lactoside and thiophenol cellobioside may be regarded as thiophenol glucosides of the normal ringed type substi-

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[4] Fischer and Delbruck, Ber., 42, 1476 (1909).

tuted by galactose and by glucose residues, respectively. This conclusion is entirely in accord with the commonly accepted constitution of the corresponding methyl glycosides due to Haworth and his collaborators[5] whose publications include a comprehensive review of the literature. As these authors examined the structure of methyl lactoside and cellobioside by the methylation method, the present work provides a direct and independent confirmation of an important part of their findings.

Experimental

Stability of B-Thiophenol Glucoside toward Aqueous Acid.—A solution of the glucoside in 0.5 *N* sulfuric acid had an initial observed reading of −3.005° in a 2-dm. tube and, after heating for two hours at 80° and for one hour at 100°, the liquid remained perfectly clear and did not smell of thiophenol. On cooling, the observed rotation was —2.995" and thiophenol glucoside was therefore stable under these conditions.

When the thioglucoside was boiled under a reflux condenser with sulfuric acid of normality 0.8 N, an initial reading of −1.240° changed to one of −1.222° in the course of three hours, while the solution acquired a faint odor of thiophenol. As complete hydrolysis to glucose and thiophenol required a change in the observed reading from −1.240 to 0.611°, that which occurred was of the order of 1%.

Thiophenol Glucoside from Thiophenol Lactoside.—Five grams of the thiophenol lactoside was dissolved in normal sulfuric acid and the solution, volume exactly 50 cc., was heated for an hour on the water-bath. The specific rotation increased during this time from $[\alpha]_D$ −38.3° (observed in a 2-dm. tube, the rotation was 7.65" to the left) to $[\alpha]_D$ −19.1° (observed **a** —3.81") but subsequent determinations were made uncertain by the presence of thiophenol. After continuing the heating for forty-five minutes, the cloudy solution was neutralized with aqueous alcoholic caustic soda and after a filtration was found to turn plane-polarized light 0.96° to the left when in a 2-dm. tube. As the total volume was now 116 cc., the observation corresponds to a specific rotation of $[\alpha]_D$ −10.66°, corrected on the assumption that the change to galactose and β-thiophenol glucoside had been quantitative. The theoretical rotation for such an equimolecular mixture is $[a]_D$ −9.56°, measured in distilled water.

The solvents were removed by evaporation under diminished pressure, the dry residue was repeatedly extracted with ethyl acetate and 2.4137 g. of fine needles was recovered from the concentrated extracts by the cautious addition of ether. The crude product, melting at 125–128° and with a specific rotation in water of $[\alpha]_D^{20}$ —65.91° (0.2105 g. in 25 cc. had α —1.115" when observed in a 2-dm. tube) was therefore recovered in 75.4% of the theoretical yield. After two recrystallizations from ethyl acetate, the preparation had a melting point of 130–132°, of 132–133° when mixed with an authentic specimen of pure β-thiophenol glucoside and a specific rotation of $[\alpha]_D^{19}$ −69.2° in water. The constants for pure β-thiophenol glucoside are m. p. 133" and $[\alpha]_D^{20}$ −70.5° in water.

Acetic anhydride and anhydrous sodium acetate acetylated the material and tetra-acetyl-β-thiophenol glucoside was recovered in 90% yield after being recrystallized from alcohol. The physical constants, m. p. 117° and $[\alpha]_D^{17}$ —18.0" in chloroform (0.6701 g. in 25 cc. had an observed reading of 0.965' to the left in a **2-dm.** tube), were in excellent agreement with those accepted as correct for tetra-acetyl β-thiophenol glucoside, m. p. 117" and $[\alpha]_D^{20}$ −17.5" in the same solvent. **A** mixture of the two specimens also melted at 117°.

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[5] Haworth and Long, J. Chem. *Soc.*, 131, 544 (1927); Haworth, Long and Plant, *ibid.*, 2809 (1927).

The residue from the hydrolysis which was insoluble in ethyl acetate was extracted with methyl alcohol to recover the reducing sugar, which slowly crystallized from the extract after the alcohol had been replaced by a little glacial acetic acid; yield, 0.826 g., or 41% of the theoretical. The crystals were those of or-galactose and without further purification displayed a mutarotation in water of $[\alpha]_D$ 140' (extrapolated) to an equilibrium rotation of $[\alpha]_D$ 77.35°, in fair agreement with the constants accepted for the pure sugar, $[\alpha]_D$ 144° to $[\alpha]_D$ 80.5' (0.4929 g. in 25 cc. gave a final observed reading of 3.051° to the right in a 2-dm. tube).

Thiophenol Glucoside from Thiophenol Cellobioside.4.7926 g. of pure β-thiophenol cellobioside was dissolved in normal sulfuric acid and the solution, volume exactly 100 cc. and having an observed rotation in a 2-dm. tube of —5.29", was heated on a steam-bath for three hours. At the end of that time the liquid was cooled, made up to its original bulk with water and shaken with a few cc. of chloroform to dissolve a trace of thiophenol and a small orange precipitate. The optical rotation of the aqueous portion had then increased to —2.29°, corresponding to a specific rotation of $[\alpha]_D^{17}$ —23.0' when calculated on the basis that the hydrolysis to glucose and thiophenol glucoside had been quantitative. The theoretical specific rotation for this mixture is $[\alpha]_D^{20}$ —21.5°, measured in distilled water.

After removing the free acid as barium sulfate, the solution was evaporated to dryness under diminished pressure and the residue was extracted ten times in succession with boiling ethyl acetate. The thiophenol glucoside isolated from the extract and once recrystallized weighed 1.505 g. or 50% of the theoretical, melted at 125–127°, at 128–129° when mixed with authentic β-thiophenol glucoside and had a specific rotation in water of $[\alpha]_D^{26}$ —65.13' (0.4578 g. in 25 cc. had an observed reading in a 2-dm. tube of 2.386" to the left). It was thus impure and was acetylated in the usual way to give an almost quantitative yield of tetra-acetyl-β-thiophenol glucoside whose melting point of 117° was not depressed by admixture with the standard substance. The specific rotation of $[\alpha]_D^{18}$ —18.25" in chloroform (0.3051 g. in 25 cc. had α —0.445' in a 2-dm. tube) was reduced to $[\alpha]_D^{18}$ —17.84' by a recrystallization from alcohol (0.4737 g. in 25 cc. of chloroform had or —0.676" in a 2-dm. tube) and thus agreed well with the standard rotation of $[\alpha]_D^{20}$ —17.5° for tetra-acetyl-β-thiophenol glucoside.

The residue from the ethyl acetate extractions failed to crystallize but yielded an osazone, decomposing at 204° when heated on the water-bath with phenylhydrazine and acetic acid. After a purification from aqueous pyridine, 0.1 g. was made up to 5 cc. with ethyl alcohol containing 40% by volume of pyridine and the solution was examined polarimetrically after having stood for eighteen hours in a 0.5-dm. tube. The observed rotation, —0.40°, was identical with that possessed by an authentic sample of glucosazone in the same circumstances.[6]

The author wishes to thank Dr. C. S. Hudson for his interest in the research and for many valuable suggestions. He also expresses his great indebtedness to the Commonwealth Fund of New York for the Fellowship which made the research possible.

Summary

1. β-Thiophenol lactoside and β-thiophenol cellobioside, on partial hydrolysis with aqueous acid, yielded a β-thiophenol glucoside identical in all respects with a specimen prepared from glucose itself.
2. It was concluded from the above evidence that the glucose resi-

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[6] Levene and LaForge, J. *Biol. Chem.*, 20,429 (1915).

due common to the thioglycosides of both these disaccharides possessed an oxygen bridge linking in the normal position.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXIII. THE PREPARATION AND THE STRUCTURE OF BETA-THIOPHENOL MALTOSIDE AND OF ITS HEPTA-ACETATE[1]

BY CLIFFORD B. PURVES

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β-Thiophenol cellobioside and β-thiophenol lactoside, according to the evidence presented in the preceding paper,[2] may be regarded as derivatives of a β-thiophenol glucoside of the normal ring structure. The two compound thioglycosides were submitted to the action of aqueous acid in such a way that glucose, or galactose, and thiophenol glucoside formed the main products of the partial hydrolysis. On examination, the specimens of thiophenol glucoside so prepared were found to be identical in all respects with one derived from acetobromoglucose and potassium thiophenate. It was this fact which led to the above conclusion, although it will be noticed that the reasoning involved the assumption that the relatively great stability of the thioglycosides toward acid hydrolysis precluded any change in their ring structure during the course of the experiment.

The examination of maltose in similar fashion was beset with the difficulties found in obtaining an adequate supply of hepta-acetyl-β-thiophenol maltoside in a pure condition. These were largely due to the unsatisfactory nature of the reaction between hydrogen bromide in glacial acetic acid-chloroform solution and maltose β-octa-acetate, which fails to result in a crystalline acetobromo derivative. This compound formed the starting point in the preparation of the thiophenol glycoside acetate. When *the* action of the hydrogen bromide solution was limited to two and one-half hours at 0°, 60% of the octa-acetate was recovered unchanged after the remainder had been condensed with potassium thiophenate, in spite of the fact that a 500% excess of the gas had been used and that similar acetates, such as those of glucose or cellobiose, give almost quanti-

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[1] Publication approved by the Director of the Bureau of Standards, U. S. Department of Commerce.

[2] The author has arranged with Dr. C. S. Hudson, under whose direction the research was carried out, that it will be included as No. XXIII in his series entitled "Relations between Rotatory Power and Structure in the Sugar Group." No. XXII was published in THIS JOURNAL, 51,3627 (1929).

tative yields of the acetobromo sugars under the same conditions. On another occasion a solution of maltose acetate and a 600% excess of hydrogen bromide were allowed to stand in solution at 20° for forty-eight hours with the result that twenty-six per cent. by weight of the acetate used was recovered as pure tetra-acetyl-P-thiophenol glucoside. The experimental conditions finally adopted for the preparation of acetobromo maltose were intermediate to those described above and were very similar to those used by Irvine and Black,[3] although the small scale to which the authors restricted the reaction was found to be unnecessary. When the directions cited in the experimental portion were adhered to with rigor, a chloroform solution of the amorphous derivative was obtained which gave a reliable yield of 49.5% by weight of crude, crystalline hepta-acetyl-β-thiophenol maltoside when condensed with potassium thiophenate in the usual way.

The crude acetylated glycoside could not be purified readily by recrystallization from chloroform and ether, and the fractions which separated from these solvents displayed a specific rotation which varied capriciously from $[\alpha]_D$ 43° to $[\alpha]_D$ 52" in chloroform. Reacetylation failed to give a homogeneous product and showed that the irregularities were not due to the partial removal of acetyl groups from the thioglycoside during the condensation. As sulfur and acetyl estimations tended to be high and low, respectively, the presence of tetra-acetyl thiophenol glucoside was inferred but whatever the nature of the impurity was, it was eventually eliminated by the careful fractional crystallization of the crude hepa-acetyl-β-thiophenol maltoside from absolute alcohol. The constants of the pure compound were found to be m. p. 93–95" and $[\alpha]_D^{27}$ $-49.0°$ in chloroform.

The molecular rotation of hepta-acetyl β-thiophenol maltoside, M_D 35,660 in chloroform, may be expressed in the manner of Hudson[4] as $B - A_{SPh}$, where B refers to the rotation of the acetylated basal chain and has the value M_D 62,700. From this the rotation of the terminal asymmetric carbon atom, A_{SPh}, in the thioglycoside acetate is seen to be of a magnitude M_D 27,040 in chloroform, which is considerably lower than the average value of M_D 30,500 deduced from the molecular rotations of the fully acetylated β-thiophenol glycosides of glucose, xylose, lactose and cellobiose.[5] In the same article, moreover, it was shown that the deviations from the mean value of A_{SPh} for these four sugars were opposite in sign but similar in magnitude to those encountered in the quantity A_{Cl}, the rotation due to the terminal asymmetric center in the corresponding acetochloro derivatives. The sum $A_{SPh} + A_{Cl}$ was therefore remarkably constant throughout the series examined and amounted to M_D 69,200 in chloro-

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[3] Irvine and Black, J. *Chem. Soc.,* 862 (1926).

[4] Hudson, THIS JOURNAL, 46,462 (1924).

[5] Purves, ibid., 51,3619 (1929).

form. β-Thiophenol maltoside acetate and acetochloro maltose supply a further illustration of the principle. for the sum $A_{\mathrm{Cl}} + A_{\mathrm{SPh}}$ (41,400[4] + 27,040) is M_{D} 68,440 in this case and agrees well with the former value.

Two attempts were made to prepare a crystalline β-thiophenol maltoside from the hepta-acetate, alcoholic ammonia being used as the deacetylating agent on one occasion and sodium methylate on the other, but both methods yielded an amorphous white solid which could not be crystallized and which was not fermented by yeast. The specific rotation of the impure thioglycoside was of the order of $[\alpha]_{\mathrm{D}}^{27}$ 38° in water but its extremely hygroscopic nature caused the determination to be of doubtful accuracy.

As thiophenol maltoside possessed such unsatisfactory physical properties, the crystalline acetate was submitted in its place to a partial hydrolysis with dilute sulfuric acid and yielded glucose and a thiophenol glucoside. This amorphous mixture was not readily separated by means of acetone or ethyl acetate and the amount of the thioglucoside recovered by the use of these solvents was only 55% of the theoretical yield. The insoluble portion was therefore fermented with yeast in order to remove the reducing sugar and when this was done a further quantity of β-thiophenol glucoside could be isolated, the total thus being increased to 71% of the theoretical. Acetylation of the material gave a pure tetra-acetyl-β-thiophenol glucoside, which was characterized with precision and found to be identical with a specimen prepared from acetobromoglucose.

β-Thiophenol maltoside, then, as well as the same derivative of cellobiose, must be regarded as β-thiophenol glucoside of the normal structure substituted in one hydroxy group by a second glucose residue. Haworth and his collaborators[5] have very recently elucidated the constitution of β-methyl maltoside by the methylation method and with the same result Their more extended investigation shows that the methyl glycosides of cellobiose and maltose differ in a stereochemical sense only in that the former is a β-glucosido-glucoside while the latter possesses the a-configuration. Such a conclusion is in full accord with the properties of the glycosides of the two disaccharides but fails to explain the sharp distinction to be observed in the behavior of their acetates toward hydrogen bromide. The amorphous nature of acetobromo maltose, together with the low yields of crystalline β-glycosides which may be prepared from it, suggests that it is the product of a more complex reaction than that which results in acetobromo cellobiose. The reason for this anomalous behavior remains obscure.

Experimental

Preparation of β-Thiophenol Maltoside Acetate.—A 50-cc. graduated glass-stoppered flask held exactly 10 g. of pure β-maltose octa-acetate, 20 cc. of chloroform and 20 cc. of a glacial acetic acid solution which contained 340 g. of hydrogen bromide

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[5] Haworth and Peat, J. *Chem. Soc.*, 3094 (1926).

per liter. After standing in a constant temperature room for eight hours at 20°, the mixture was made up to the mark with chloroform, shaken and found to have a positive reading of 74.1' on the polarimeter when observed in a 2-dm. tube. The specific rotation of the acetobromomaltose was therefore $[\alpha]_D$ 180.1°, when calculated on the basis that its formation from the octa-acetate had been quantitative. The acids were then removed from the solution by washing, thrice repeated, with ice water and the wet chloroform residue containing the acetobromo sugar was run into a mixture of 1.65 cc. (10% excess) of thiophenol and 21 cc. of 0.7 N alcoholic potassium hydroxide (the theoretical amount). Warming on the water-bath for forty minutes completed the condensation. After washing potassium bromide, thiophenol and alcohol from the liquor with very dilute aqueous sodium bicarbonate, the chloroform solution was dried over calcium chloride and evaporated to a thin sirup, which was straightway taken up in 30 cc. of cold alcohol. Hepta-acetyl-β-thiophenol maltoside readily crystallized in the presence of a nucleus when 5 to 6 cc. of water was added and the solution was steadily scratched; yield, 4.95 g., m. p. 90–93°, $[\alpha]^{19}_D$ 44.64' (0.3170 g. in 25 cc. of chloroform gave an observed reading of 1.132° to the right when in a 2-dm. tube).

In order to purify the thioglycoside acetate, the product from several condensations, 13 g., was allowed to separate from an initial volume of 160 cc. of absolute alcohol in five fractions, the properties of which were as follows.

FRACTION 1.—Slender felted needles, apparently homogeneous; weight, 5.31 g.; 0.3223 g. required 30.06 cc. of decinormal caustic soda in an acetyl determination, the calculated value being 30.99 cc.; 0.2942 g. gave 0.0984 g. of barium sulfate; found, S, 4.59.

FRACTION 2.—Similar in crystalline form to the above; weight, 4.40 g.; 0.3233 g. took 31.27 cc. of decinormal alkali in an acetyl estimation where theory demands 31.09 cc.; 0.5534 g. gave 0.1795 g. of barium sulfate; found, S, 4.46.

FRACTION 3.—Similar in crystalline form to the above; weight, 2.04 g.; 0.2841 g. required 27.56 cc. of decinormal alkali in place of 27.32 cc.

FRACTION 4.—A mixture of slender needles with shorter, stouter prisms; weight, 0.65 g.; 0.3065 g. took 27.74 cc. of decinormal alkali in place of 29.47 cc. required by theory; 0.3033 g. gave 0.1120 g. of barium sulfate; found, S, 5.07.

FRACTION 5.—A small, discolored residue which crystallized completely as short, pointed prisms some weeks later. Hepta-acetyl thiophenol maltoside requires S, 4.39.

Fractions 2 and 3, which possessed satisfactory analytical figures, also agreed in their specific rotation (found, $[\alpha]_D$ 48.83°, 48.85" in chloroform; 0.3072 *g.* in 25 cc. had *a* 1.200'; 0.2966 g. had *a* 1.159° to the right in a 2-dm. tube). These fractions were therefore recrystallized together from alcohol as fine clusters of square-ended very slender prisms, soluble in petroleum ether, readily so in other organic solvents and with a specific rotation in chloroform of $[\alpha]^{27}_D$ 49.09°, or substantially the same as before (0.2213 g. in 25 cc. gave an observed reading of 0.869' to the right in a 2-dm. tube). Pure hepta-acetyl-β-thiophenol maltoside therefore possessed a specific rotation in chloroform of $[\alpha]^{27}_D$ 49.0°.

Fraction 1, after recrystallization and rejection of the first portion of 1 g. to separate, also yielded the pure thioglycoside acetate with the correct melting point of 93–95" and an accurate specific rotation (found, $[\alpha]^{22}_D$ 48.59'; 0.5217 g. in 25 cc. of chloroform gave an observed reading of 2.028' to the right in a 2-dm. tube). Thus 10.4 g. of pure hepta-acetyl thiophenol maltoside was obtained from 13 g. of the crude material, or from 26.3 g. of pure maltose octa-acetate. The yield was therefore about 37% of the theoretical.

Thiophenol Glucoside from **Hepta-acetyl β-Thiophenol** Maltoside. —Exactly 4 g. of the acetate was heated at 90° in a 100-cc. flask with 50 cc. of normal sulfuric acid and about 30 cc. of alcohol, which was just sufficient to give a clear solution. As the acetyl groups were removed during the hydrolysis, it was possible to replace this alcohol with distilled water as it evaporated, without causing the solution to become cloudy. Eight hours of heating sufficed to hydrolyze the thioglycoside, whereupon the volume was increased to the 100-cc. mark with water, a trace of thiophenol was extracted from the cold, cloudy solution with 1 cc. of chloroform and the clear aqueous portion was found to have a rotation of $-0.66°$, observed in a 2-dm. tube. This reading corresponds to a specific rotation of $[\alpha]_D$ $-13.3°$ on the assumption that the hydrolysis to β-thiophenol glucoside and glucose had been quantitative and may be compared with the theoretical rotation of $[\alpha]_D$ —21.5" for this mixture, measured in distilled water.

After the neutralization of the free acids with calcium carbonate, the filtered liquor was evaporated to complete dryness at 60° and the residue was extracted three times with acetone. The extract deposited a stiff sirup when concentrated and the portion which remained dissolved was crystallized from ethyl acetate after its recovery; 0.823 g. of crystalline β-thiophenol glucoside was so obtained m. p. 121–127°, raised to 129–131° by several purifications from ethyl acetate. A mixture of the substance with authentic thiophenol glucoside, m. p. 133°, melted at 131°, while its specific rotation was $[\alpha]_D$ —64.0" in water (0.2016 g. in 25 cc. had α $-1.032°$ when a 2-dm. tube was used). The whole of the original product which was not soluble in ethyl acetate was then united, freed from inorganic salts as far as possible by solution in methyl alcohol and fermented with yeast in 20 cc. of water after all traces of organic solvents had been removed. No glucose remaining in the solution four days later, a filtration through charcoal and a clarification with basic lead acetate were followed by the evaporation of the liquor to dryness under diminished pressure and by the extraction of the residue with ethyl acetate. The thiophenol glucoside which crystallized from the extract weighed 0.25 g. and increased the total yield of the crude material to 1.073 g., or 71.7% of the theoretical.

The acetylation of the thiophenol glucoside with acetic anhydride and pyridine, followed by recrystallization of the acetate from 95% alcohol, gave an almost quantitative yield of pure tetra-acetyl-β-thiophenol glucoside of the usual variety, m. p. 116"; mixed m. p. with an authentic specimen, 116° and $[\alpha]^{20}_D$ —18.4' in chloroform (0.4585 g. in 25 cc. and in a 2-dm. tube had a levorotation of 1.070°), thus agreeing with the standard constants, m. p. 117°, and $[\alpha]^{20}_D$ $-17.5°$, for this substance.

β-Thiophenol Maltoside.—A solution of 0.05 g. of metallic sodium in 5 cc. of absolute methyl alcohol was added to one of 8 g. of pure hepta-acetyl-p-thiophenol maltoside dissolved in 20 cc. of the same solvent.[7] The odor of methyl acetate was strong two days later, when the solution was evaporated to leave a colorless sirup which would not crystallize. The amorphous product was extremely soluble in water, methyl and ethyl alcohols, but dissolved sparingly in ethyl acetate and in cold propyl alcohol. Prior to analysis the β-thiophenol maltoside was heated at 100° (0.1 mm.) for several hours and assumed the form of an extremely hygroscopic glass with a specific rotation of $[\alpha]^{27}_D$ 38.12' in water (0.2339 g. in 25 cc. gave an observed reading of 0.357' to the right in a 1-dm. tube).

The author desires to thank the Commonwealth Fund of New York for the Fellowship which made possible his participation in the work. He also expresses his deep indebtedness to Dr. C. S. Hudson for many valuable suggestions.

Summary

1. Hepta-acetyl-β-thiophenol maltoside was synthesized from acetobromomaltose and potassium thiophenate and the constants of the pure compound were found to be m. p. 93–95" and $[\alpha]^{27}_D$ 49.0" in chloroform.

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[7] Zemplén and Pacsu, *Ber.*, 62, 1613 (1929).

2. When submitted to a partial hydrolysis with aqueous acid, hepta-acetyl-β-thiophenol maltoside yielded glucose and β-thiophenol glucoside of the normal ring structure. β-Thiophenol maltoside may accordingly be regarded as ordinary β-thiophenol glucoside substituted by a second glucose residue.

3. β-Thiophenol maltoside was obtained as a very hygroscopic glass with an approximate specific rotation of $[\alpha]_D^{27}$ 38° in water.

WASHINGTON, D. C.

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

PREPARATION OF BENZOYLACETIC ESTER

BY R. L. SHRINER AND A. G. SCHMIDT

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The usual method given for the preparation of benzoylacetic ester is the Claisen condensation[1] of ethyl acetate with ethyl benzoate. A yield of 33% is reported but all attempts to duplicate this yield have failed. A study of this condensation was made by Marvel and Shiao[2] who found that the best yield obtainable by this method was 18%. In many runs the reaction mixture turned brown, puffed up and decomposed entirely giving very little or no product at all. A similar condensation with methyl piperonylate[3] gave yields ranging from 20 to 35%.

Since benzoylacetic ester would be an extremely useful reagent if it were readily obtainable, a search was made for other methods of preparation. The present communication is a report on the preparation of benzoylacetoacetic ester and its partial hydrolysis to benzoylacetic ester.

Benzoylacetoacetic ester was prepared in the usual way by the reaction between benzoyl chloride and the sodium derivative of acetoacetic ester. It was found possible to raise the yield of product from 50 to 75% and to shorten the time materially by using a slight excess of benzoyl chloride in benzene as the medium for the reaction.

The primary hydrolysis of benzoylacetoacetic ester may take place in three different ways

$$\left.\begin{matrix}C_6H_5CO\\ CH_3CO\end{matrix}\right\rangle CHCOOC_2H_5 + H_2O \longrightarrow \begin{cases} C_6H_5COCH_2COOC_2H_5 + CH_3COOH \\ CH_3COCH_2COOC_2H_5 + C_6H_5COOH \\ CH_3COCH_2COC_6H_5 + C_2H_5OH + CO_2 \end{cases}$$

Complete hydrolysis, of course, will lead to the formation of benzoic acid, acetophenone, acetone or acetic acid and the final products obtained will depend on the conditions of hydrolysis, which evidently must be carefully adjusted in order to favor the first reaction.

The different methods reported in the literature for accomplishing this

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[1] Claisen, *Ber.*, 20, 646 (1887).

[2] Shiao, B. S. "Thesis," University of Illinois, 1923.

[3] Shriner and Kleiderer, THIS JOURNAL, 51, 1269 (1929).

hydrolysis were tried. The most promising one was a short time hydrolysis with ammonia and ammonium chloride.[4] Claisen carried out this hydrolysis on the crude sodium salt obtained by the action of benzoyl chloride on acetoacetic ester and sodium ethylate. In the present study the pure benzoylacetoacetic ester was isolated first and then subjected to hydrolysis under the influence of varying concentrations of ammonia and ammonium chloride. The results of these experiments are summarized in Table I.

TABLE I

EFFECT OF VARYING CONCENTRATIONS OF AMMONIA AND AMMONIUM CHLORIDE ON THE HYDROLYSIS OF BENZOYLACETOACETIC ESTER

Run	Benzoyl-acetoacetic ester, g.	Water, cc.	NH_4Cl, g.	NH_4OH, cc. (sp. gr. 0.9)	Temp., °C.	Time, min.	Yield of benzoyl-acetic ester g.	%
1	40.0	100	9	10	40	10	11	34.3
2	58.5 (0.25 mole)	150	16	20	40	10	23	47.9
3	58.5	150	16	40	40	10	21	43.8
4	58.5	150	32	20	40	10	29	60.3
5	58.5	150	32	10	40	10	37.5	78.1
6	58.5	150	32	none	40	10	..	..

Run No. 1 was made according to Claisen's directions and resulted in a yield of 34%, although Claisen[5] claims 64–67% yields. A comparison of Runs 2 and 3 indicates that an increase in the ammonia concentration decreases the yield. An increase in ammonium chloride is beneficial up to a certain point. Run No. 6 resulted in the production of large quantities of benzoic acid. The optimum conditions are those given in No. 5. It was also found that the use of a higher temperature or longer time of hydrolysis resulted in lower yields.

It is evident that this same method can be applied to the preparation of substituted benzoylacetic esters.

Experimental

Preparation of Benzoylacetoacetic Ester.—Claisen[4] prepared this compound by adding benzoyl chloride slowly to a solution of acetoacetic ester in a sodium ethylate solution. Other investigators[6] have prepared the benzoylacetoacetic ester by adding metallic sodium to an ether solution of acetoacetic ester and then adding benzoyl chloride. The first method is objectionable because considerable amounts of ethyl benzoate are formed and the second requires a long time because of the slowness with which the sodium reacts with the acetoacetic ester. By using benzene and warming the mixture the time of preparation is considerably shortened. The optimum conditions are as follows.

In a 5-liter flask fitted with a mechanical stirrer and reflux condenser were placed

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[4] Claisen, *Ann.*, 291, 71 (1896).

[5] From a consideration of Claisen's experimental data it is evident that two runs were combined in order to obtain the above yield. Attempts to duplicate Claisen's work by several different workers have given yields ranging from 29 to 34%.

[6] Bonné, *Ann.*, 187, 1 (1877); Fischer and Bülow, *Ber.*, 18, 2131 (1885); Nef. *Ann.*, 266, 99 (1891); Pechmann, *Ber.*, 25, 1046 (1892).

4.5 liters of dry benzene, 260 g. (2 moles) of acetoacetic ester and 46 g. (2 moles) of sodium. The mixture was stirred and allowed to reflux gently for twenty-four hours. The solution was then cooled slightly and 350 g. (2.5 moles) of benzoyl chloride added slowly over a period of three hours. The mixture was refluxed with stirring for eight hours. It was then cooled to room temperature and 500 g. of cracked ice added. After shaking thoroughly the benzene layer, which contains the benzoylacetoacetic ester, was separated and the benzene distilled. The residue was then distilled from a Claisen flask with modified side-arm and the fraction boiling at 177–181° at 20 mm. collected; yield, 350 g. or 74.8% of the theoretical.

Hydrolysis of Benzoylacetoacetic Ester.—The first hydrolysis recorded in Table I was made according to Claisen's directions.[4] The remaining hydrolyses were made in accordance with the procedure outlined below, the only variables being the amounts of ammonia and ammonium chloride. The amounts stated in the following procedure are those of Run 5 which represents the optimum conditions.

Thirty-two grams (0.6 mole) of ammonium chloride was dissolved in 150 cc. (8.3 moles) of water and 10 cc. (0.10 mole) of ammonia (sp. gr. 0.9) added. The solution was warmed to 40° and 58.5 g. (0.25 mole) of benzoylacetoacetic ester added. The solution was kept at 40° for ten minutes and then cooled rapidly by placing the flask in an ice-bath. It was extracted twice with 100 cc. of ether and the ether solution dried with anhydrous magnesium sulfate. The ether was distilled and the residue distilled in *vacuo;* yield, 37.5 g. (78.1% of the theoretical) of benzoylacetic ester boiling at 165–169° at 20 mm.; sp. gr. at 20°, 1.1098; n_{D}^{20} 1.5498.

Summary

The preparation and partial hydrolysis of benzoylacetoacetic ester to give benzoylacetic ester have been studied and optimum conditions worked out.

URBANA, ILLINOIS

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

IDENTIFICATION OF AMINES.
V. DERIVATIVES OF TERTIARY AMINES

BY C. S. MARVEL, E. W. SCOTT AND K. L. AMSTUTZ

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Solid derivatives of tertiary amines suitable for identification purposes are not always available. The methiodides, picrates, chloroplatinates, chloro-aurates and simpler salts such as the hydrochlorides, hydrobromides, etc., are at times useful but no one derivative is generally applicable to a wide number of amines. These derivatives have the common fault of melting with some decomposition and the temperature of decomposition is usually dependent on the rate of heating.

The most characteristic reaction of tertiary amines is the formation of quaternary ammonium compounds by addition to the nitrogen atom. It is generally true that the greater the proportion of the hydrocarbon part of the molecule in a quaternary ammonium salt, the more likely the compound is to have a sharp melting point. With this idea in mind, the addition of benzyl chloride, *p*-nitrobenzyl chloride and phenacyl chloride to a large number of tertiary amines was tried. The results were disappointing. Benzyl chloride reacted with four common amines to give new derivatives which were easily prepared and crystallized, but many products were too difficult to purify. *p*-Nitrobenzyl chloride was not at all satisfactory. Phenacyl chloride reacted with pyridine and α-picoline to give quaternary ammonium salts melting at 113 and 157°, respectively, but did not seem to show promise of general usefulness.

Several cases of the formation of quaternary ammonium compounds from tertiary amines and esters of arylsulfonic acids have been reported. A patent[1] describes the addition products of several quinoline derivatives with methyl and ethyl *p*-toluenesulfonates, and ethyl p-bromotoluenesulfonates. The melting points of these derivatives were reported as follows: 1-ethyl-2-methylquinolinium p-toluenesulfonate, 105°; 1-ethyl-2,6-dimethylquinolinium p-toluenesulfonate, 120°; 1,2-dimethylquinolinium *p*-toluenesulfonate, 134'; 1-ethyl-2-methylquinolinium p-bromotoluenesulfonate, 142°. More recently Simon and Frerejacques[2] observed that the methyl esters of several complex arylsulfonic acids combined with hexamethylenetetramine and some other complex tertiary amines to give products with sharp melting points. Rodionow[3] has described trimethylphenylammonium benzenesulfonate, m. p. 180–181°; dimethylethylphenylammonium p-toluenesulfonate, m. p. 48-49 °; trimethylphenylammonium p-toluenesulfonate, m. p. 160–161°, and the methyl *p*-toluenesulfonate derivatives of several alkaloids.

The properties of these addition products suggested that methyl p-toluenesulfonate might prove to be a general reagent for use in identifying tertiary amines. A number of compounds of this type have been prepared and characterized. The reagent was found to be particularly useful with ring nitrogen compounds. Practically all of the pyridine and quinoline derivatives which were prepared, were well suited for identification purposes. However, it is less useful for the other types of amines studied as too many derivatives failed to crystallize.

Other experiments were made in the use of methyl *p*-bromobenzenesulfonate and methyl methanesulfonate. Each of these reagents gave some crystalline derivatives but none was useful where the methyl *p*-toluenesulfonate was unavailable,

Experimental Part

The addition compounds which are described in the tables were all prepared by mixing 1 g. of the amine and 2 to 3 g. of the reagent (benzyl

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[1] German Patent 170,048, *Chem. Zentr.*, I, 1857 (1906).

[2] Simon and Frerejacques, *Compt.* rend., 178, 945 (1924).

[3] Rodionow, Bull. *soc. chim.*, [4] 39, 305 (1926).

chloride, methyl p-toluenesulfonate, methyl *p*-bromobenzenesulfonate or methyl methanesulfonate) in 10 cc. of dry benzene. The mixture was heated to boiling for about thirty minutes, cooled and filtered. The product was recrystallized by dissolving in the least amount of boiling ethyl alcohol and adding ethyl acetate until the material began to precipitate. The melting points given in the table were taken on compounds which had been purified to constant melting point.

TABLE I

NEW DERIVATIVES OF TERTIARY AMINES WITH BENZYL CHLORIDE

Amine	M. p., °C.	Cl calcd., %	Cl found, %
Diethylaniline	104	12.86	12 68
Dimethyl *p*-toluidine	171	13.60	13.04
6-Methylquinoline	209	13.15	13.04
Tri-*n*-butylamine	185	11 33	11.45

TABLE II

NEW DERIVATIVES OF TERTIARY AMINES AND SULFONIC ESTERS

Amine	Reagent, methyl ( )-sulfonate	M. p., °C.	S calcd., %	S found, %
Pyridine	p-Toluene	138–139	12 08	11.93
a-Picoline	p-Toluene	149–150	11.45	11.31
a-Chloropyridine	*p*-Toluene	119–120	10.68	10.78
Quinoline	p-Toluene	125–126	10.15	9.98
2-Methylquinoline	p-Toluene	161[a]	9 73	9.48
6-Methylquinoline	p-Toluene	153–154	9.73	9.87
6-Chloroquinoline	p-Toluene	142–143	9.10	9.21
6-Bromoquinoline	*p*-Toluene	150–152[b]	8.12	8.12
2,6-Dimethylquinoline	p-Toluene	175	9.32	9.54
Isoquinoline	p-Toluene	163	10.15	10.05
Dimethylaniline	p-Toluene	161[c]	....	...
Dimethyl-p-toluidine	*p*-Toluene	85	9.98	10.21
Di-n-butylaniline	p-Toluene	180	8.19	7.98
Tri-*n*-amylamine	*p*-Toluene	76–80[d]	7.75	8.16
Dimethylaniline	*p*-Bromobenzene	218–220	8.60	8.23
Dimethylaniline	Methane	192° (dec.)	13.85	14.00

[a] This melting point is higher than that recorded in the patent literature **(Ref. 1)**. [b] This product seemed to soften somewhat at 95°. [c] Ref. 3. [d] The amount available was not great enough to permit crystallization to constant melting point.

Methyl p-toluenesulfonate gave oily products with the following amines: diethylaniline, di-n-propylaniline, di-isopropylaniline, ethylbenzylaniline, diethylallylamine, di-n-butylallylamine and nicotine.

Summary

1. Benzyl chloride, p-nitrobenzyl chloride, phenacyl chloride, methyl p-toluenesulfonate, methyl p-bromobenzenesulfonate and methyl methanesulfonate have been investigated as reagents for use in the preparation of derivatives for the identification of common tertiary amines.

2. Methyl p-toluenesulfonate has been found to be a fairly general reagent and to be particularly useful in the case of ring nitrogen compounds.

URBANA, ILLINOIS

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXIV. RING MIGRATION IN THE GLYCEROL CYCLIC ACETALS. BEHAVIOR OF PARA-NITROBENZYLIDENE GLYCEROL[1]

BY HAROLD HIBBERT, MURIEL E. PLATT AND NEAL M. CARTER

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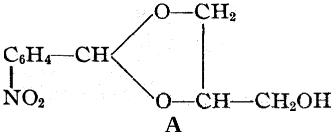
The close structural relationships existing between cyclic acetals on the one hand and carbohydrates, anhydro sugars and polysaccharides on the other has been emphasized frequently in this series of communications.[2] The present investigation deals with the interconversion of the 5- and 6-membered p-nitrobenzylidene glycerols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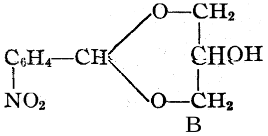
B

It has been found, in accordance with previous work carried out on the benzylidene and methylidene glycerols,[3,4] that in the presence of a trace of dry hydrochloric acid gas the six-membered derivative (B) is readily converted into an equilibrium mixture of the five- and six-membered isomers. By carrying out the reaction at 100° for one and a half hours, an equilibrium is apparently reached in which the proportion of 6:5-membered acetals is represented by 1:2.

In a second series of experiments, carried out by heating the crystalline six-membered acetal (B) with dilute hydrochloric acid ($N/10$) in a sealed tube at 100° for varying lengths of time, it was found that after about an hour an equilibrium mixture was obtained in which the six- and five-membered rings were present in the ratio of 0.37:1. In this series of experiments certain discrepancies came to light in that, for example, discordant results were obtained if the crystalline 6-membered acetal recovered

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[1] Constructed from the thesis of Muriel E. Platt as presented to the Graduate School of McGill University in June, 1929, in candidacy for the degree of Master of Science.

[2] Hibbert and co-workers, THIS JOURNAL, 45, 734 (1923); 50, 2235, 2242 (1928); 51,620 (1929).

[3] Hibbert, Whelen and Hill, *ibid.*, 50,2235 (1928).

[4] Hibbert and Carter, *ibid.*, 50,3120 (1928).

from one equilibrium experiment was used, without complete purification, for the following one. The explanation of this is probably to be found in the fact that the *p*-nitrobenzylidene glycerols exist in cis and trans forms. It was also found that while equilibrium was established after approximately a one-hour period, that this was far from being realized when the time interval fell slightly below sixty minutes. Using, however, the same pure, crystalline, p-nitrobenzylidene six-membered isomer (m. p. 93.5°) for each experiment, values were found as represented graphically on the accompanying curve.

The results obtained indicate the pronounced tendency of each of the two rings to pass over into an equilibrium mixture in presence of acid, and serve not only as a further illustration of "Michael's Partition Principle," but also for the necessity of avoiding acid media when conducting experiments designed to throw light on the structure of glycerol acetals, and by analogy, on carbohydrates, anhydro sugars and polysaccharides.

Experimental

Preparation of **1,3-*p*-Nitrobenzylidene** Glycerol (2-p-Nitrophenyl-5-m-dioxanol).—The procedure adopted for the preparation of this compound was that developed by Hibbert and Carter.[5] A mixture of 50 g. of p-nitrobenzaldehyde, 33.1 g. of glycerol (3% excess over the theoretical amount) and three drops of 40% sulfuric acid as catalyst gave 29.3 g. of the 1,3-*p*-nitrobenzylidene glycerol melting at 93°; yield, 58 8%.

Interconversion of the 5- and 6-Membered Rings by the Action of Dry Hydrogen Chloride.—Two-gram samples of freshly recrystallized 1,3-*p*-nitrobenzylidene glycerol were mixed with 0.01% of their weight of dry hydrogen chloride in sealed tubes and allowed to stand for one and a half hours at 100° The product, in each case, was then cooled to room temperature, diluted with 20 cc. of benzene and the acid neutralized with fused pstassium carbonate. The solvent was removed under reduced pressure. The weight of the mixture of 1,3- and 1,2-acetals recovered was 1.2 g. The mixture was taken up in benzene and allowed to crystallize at 0° in order to isolate the 6-membered isomer. The weight of the crystalline unchanged 1,3-material was 0.4 g. The ratio of 6- to 5-membered acetal thus obtained is approximately 1:2. The low yields are presumably due to ring scission and formation of p-nitrobenzaldehyde and glycerol, as shown later in the experiment with $N/10$ hydrochloric acid.

Interconversion of the 5- and 6-Membered Cyclic Acetal Rings by Very Dilute Hydrochloric Acid.—Five-gram samples of 1,3-*p*-nitrobenzylidene glycerol, to which had been added 0.4 g of $N/10$ hydrochloric acid (thus introducing the theoretical quantity of water necessary for hydrolysis of the sample) were shaken vigorously and continuously in sealed ampules at 100° for varying lengths of time. This was carried out as follows. The crystalline isomer was melted before the acid was added, the ampule sealed and then placed in the shaking apparatus. At the expiration of the given time interval, the ampule was immediately plunged into a cooling bath (—12") to prevent further reaction. Those samples which had been heated for periods of fifteen and thirty minutes, respectively, solidified on cooling, while those heated for a longer period of time yielded a very viscous oil, thus indicating a partial conversion to the liquid isomer. The contents in each case were dissolved in 250 cc. of benzene, the trace of acid present was neutralized by shaking with 1 cc. of a dilute solution of potassium

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[5] Hibbert and Carter, THIS JOURNAL, **50**, 3376 (1928).

bicarbonate, the benzene solution cooled to 10° (to prevent any change in the equilibrium) and then shaken with a cold saturated solution of sodium bisulfite to remove the *p*-nitrobenzaldehyde. The formation of an addition product indicated that some of the latter had been formed during the reaction. The free glycerol, which is insoluble in benzene, remained in the mother liquor. After drying the benzene solution over solid potassium carbonate, the solvent was removed under diminished pressure and the total amount of the 5- and 6-membered acetals determined.

The separation of the two isomers was carried out by dissolving the product in 25 cc. of warm benzene and cooling the solution for two hours at −12°. The frozen mixture was allowed to stand at room temperature for half an hour, the crystals of the 6-membered acetal filtered off at room temperature, dried and weighed. The weight of the 5-membered acetal formed was determined by difference and the ratio of 6- to 5-membered acetal calculated. The solubility of the 6-membered acetal in benzene at 22° is slight, namely, one part in one hundred and fifty.

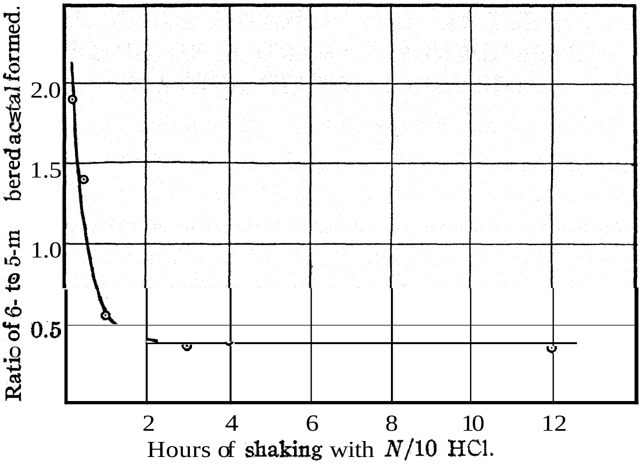

Fig. 1.

The results of the experiments are given in Table I and shown graphically on the accompanying curve (Fig. 1).

Table I

Results of Experiments

Time of heating, hrs.	0.25	0.5	1	3	4	6	12
Wt. of sample, g.	5	5	5	5	5	5	5
Comb. wt. of acetals, g.	3.4	3.1	3.6	3.3	3.35	3.6	3.1
6-Membered acetal, g.	2.25	1.8	1.3	0.9	0.9	1.0	0.8
5-Membered acetal, g.	1.15	1.3	2.3	2.4	2.45	2.6	2.3
Equil. ratio, 6:5 rings	1.9:1	1.4:1	0.56:1	0.37:1	0.38:1	0.38:1	0.35:1

Summary

1. The six-membered cyclic acetal, *p*-nitrobenzylidene glycerol, is converted, in the presence of dry hydrochloric acid gas at 100°, into an equilibrium mixture of itself with the five-membered isomer, the ratio of the former to the latter being 1:2.

2. Under similar conditions but using dilute hydrochloric acid at 100°, an equilibrium is obtained after about one hour in which the ratio of six- to five-membered acetal is 0.37:1.

3. The results indicate the ease of transformation of oxygen rings in cyclic acetals and, by analogy, point to similar conditions in the case of furanose and pyranose rings in carbohydrates, anhydro sugars and polysaccharides.

MONTREAL, CANADA

[COMMUNICATION PROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES OF REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXV. METHYLATION PROCESSES AND TENDENCY TOWARD RING SHIFT IN GLYCEROL CYCLIC ACETALS

BY HAROLD HIBBERT, MURIEL E. PLATT[1] AND NEAL M. CARTER

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In the methylation of sugars and their derivatives two methods have been employed: (1) the use of silver oxide and methyl iodide, as first originated by Purdie and developed with so much success by Irvine,[2] and (2) the use of dimethyl sulfate and sodium hydroxide, developed by Denham and Woodhouse[3] in the methylation of cellulose, and later applied by Haworth[4] in the methylation of sugars.

The silver oxide method has had a very wide application, the reaction being carried out in neutral solvents. Thus methylated aldosides, obtained by treating glucosides dissolved in methyl alcohol, with methyl iodide and dry silver oxide yielded on hydrolysis the methyl ethers of the respective aldoses.

It has been established that under these mild experimental conditions profound changes, such as racemization, the Walden Inversion or the interconversion of glucosides (α- and β-forms) do not occur. On the other hand, conclusive evidence, to some extent, is lacking as to the total absence of (a) the migration of a methyl group and (b) ring scission and ring migration.

The employment of the expensive alkyl iodides and silver oxide, as well as the necessity for finding a suitable solvent for the carbohydrate in the initial stages of the reaction, prevented a wide and general application of

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[1] Constructed from the thesis of Muriel E. Platt as presented to the Graduate School of McGill University in June, 1929, in candidacy for the degree of Master of Science.

[2] Purdie and Irvine, J. Chem. *Soc.*, 83,1021 (1903).

[3] Denham and Woodhouse, *ibid.*, 103, 1735 (1913).

[4] Haworth, *ibid.*, 107, 8 (1915).

the process, and restricted the further study of the alkylated disaccharides. Haworth, therefore, applied the dimethyl sulfate method, which Denham and Woodhouse had used with cellulose, to the sugars with satisfactory results. Inasmuch as Haworth states,[5] "There are eight available hydroxyl groups in a dihexose. These may be protected by simple methylation with methyl sulfate and dilute alkali, but the conditions must be so chosen that when the disaccharide is sensitive to acids, as is sucrose, the alkali should always be present in excess. On the other hand, since other disaccharides are adversely affected by alkali, it is necessary to ensure, particularly during the earlier stages of the methylation process, that alkalinity does not develop. These conditions can be controlled by maintaining an excess of methyl sulfate during the addition of dilute alkali solution," . . . it is evident that he assumes no ring scission or ring shift (for example, a furanose into a pyranose derivative) in the presence of an acid medium. The various researches carried out by Hibbert and co-workers on cyclic acetal formation indicate clearly, however, the very labile character of such rings and the remarkable ease with which one is transformed into the other in the presence of a trace of acid. It is, therefore, of considerable interest to ascertain whether in the case of a cyclic acetal characterized by ease of ring scission and ring migration, such changes occur during the process of methylation by means of dimethyl sulfate under varying conditions of acidity and alkalinity.

It is now known that in the condensation of acetone with glucose in the presence of a small amount of hydrochloric acid, a ring shift actually occurs[6] and, since benzylidene glycerol is very similar to an acetone sugar with regard to its ease of hydrolysis in acid media, series of methylation experiments on crystalline 1,3-benzylidene glycerol, using dimethyl sulfate and alkali as the methylating agent, were undertaken with a view of determining: (a) the yield of crystalline 1,3-benzylidene-glycerol-2-methyl ether and (b) the possibility of ring shift with consequent formation of the *liquid*, isomeric 1,2-benzylidene-glycerol-3-methyl ether.

The structure of both of these ethers has been definitely determined.[7] The methylation of the 1,3-derivative was carried out under two sets of conditions: (a) in a reaction mixture containing at the start an excess of dimethyl sulfate, that is, in an acid medium, and (b) in a reaction mixture which was kept distinctly alkaline at all stages.

Reaction in Acid Medium.—The only product obtained when an excess of dimethyl sulfate was used was a small amount of benzaldehyde formed by hydrolysis of the 1,3-benzylidene glycerol by the dimethyl sulfate.

Reaction in Alkaline Medium.—Under these conditions 1,3-benzylidene-

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[5] Haworth, "Constitution of Sugars," London, 1929, p. 55.

[6] Anderson, Charlton and Haworth, J. Chem. *Soc.*, 1329 (1929).

[7] Hibbert and Carter, THIS JOURNAL, 50, 3376 (1928).

glycerol-2-methyl ether and unchanged original product were obtained when the methylation was carried out in the presence of alkali at 30°, but no 1,2-benzylidene-3-methyl ether could be detected.

At lower temperatures small amounts of unchanged original product only were recovered.

A distinct odor of benzaldehyde was noticed in all the reaction mixtures, indicating that the sensitive acetal ring undergoes hydrolysis even under these conditions; this is probably the reason for the low yields of total recoverable crystalline products. Some of the benzaldehyde may also have been oxidized to benzoic acid, which would have been retained as the sodium salt, although none of the acid was obtained on neutralization and extraction of the aqueous reaction mixture. An attempt to isolate the *liquid* 1,2-benzylidene glycerol isomer (formed by ring shift of the 1,3-isomer) from the mother liquor, obtained after removal of the crystalline 6-membered form, through the formation of its *p*-nitrobenzoate,[8] was unsuccessful, no evidence being obtained of its formation in the methylation process.

The results of these experiments would seem to indicate that, with an alkali-insoluble acetal such as 1,3-benzylidene glycerol, methylation does not take place readily, but that no ring shift occurs under alkaline conditions. However, extensive hydrolysis to glycerol and benzaldehyde readily occurs in both acid and alkaline media.

Experimental

Preparation of 1,3-Benzylidene Glycerol.—Benzylidene glycerol was prepared from benzaldehyde and glycerol by the method previously described.[7] One hundred thirty-eight grams of benzaldehyde, 131 g. of glycerol and six drops of concentrated hydrochloric acid yielded 145 g. of a mixture of isomeric benzylidene glycerols. The 1,3-isomer isolated had a melting point of 80°.

Methylation of 1,3-Benzylidene Glycerol with Dimethyl Sulfate Solution.—To 14 g. of freshly recrystallized 1,3-benzylidene glycerol, dissolved in 62.5 g. (five times the theoretical amount) of dimethyl sulfate at 0°, 90 cc. of a 40% sodium hydroxide solution (five times the theoretical amount) was added slowly through a buret. After five hours of constant stirring at 0°, two layers separated, after which the mixture was stirred for two hours at room temperature. The aqueous layer which separated out was strongly alkaline. The mixture was extracted with ether, the ether extract separated from the aqueous layer and the latter then extracted several times. The combined ether extracts were dried over fused potassium carbonate and the ether distilled off. The residue on fractionation yielded 3 cc. of benzaldehyde. No crystals could be obtained from the residue when it was taken up in benzene–petroleum ether (2:1), this being the method usually employed for the separation of these isomers.

Methylation of 1,3-Benzylidene Glycerol with Dimethyl Sulfate in Alkaline Solution. Methylation at 0°.—To 13.9 g. of the freshly recrystallized 6-membered acetal dissolved in 20 cc. of methyl alcohol and cooled to 0°, 90 cc. of a 40% sodium hydroxide solution (a little more than five times the theoretical amount) and 62.5 g. of dimethyl

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[8] Hibbert and Carter, THIS JOURNAL, 50, 3120 (1928).

sulfate (five times the theoretical amount) were added slowly from different burets, using phenolphthalein as an indicator, in order to be certain that the mixture remained slightly alkaline A precipitate which was present from the start proved to be sodium sulfate, which was insoluble in the aqueous alcoholic solution. After stirring for four hours at 0°, the product was filtered, the filtrate extracted with ether and the extract dried over potassium carbonate. On evaporation of the solution to about 15 cc. and cooling, crystals separated out. The product was taken up in benzene–petroleum ether (2:1) and cooled. Two grams of crystals (14.5% of original) was separated with a melting point of 80°, that is, the melting point of the original acetal.

Methylation at 30°.—The above experiment was repeated at 30° using 49 g. of the 1,3-acetal, 160 g. of sodium hydroxide (in 40% solution) and 175 g. of dimethyl sulfate. After stirring for four hours, a stream of carbon dioxide was bubbled through the mixture for two hours in order to change any sodium derivative of the unchanged acetal which might have been formed during the reaction back to the ether-soluble free acetal. The product was then extracted with ether and the ether removed under reduced pressure. The residue was taken up in a mixture of benzene and petroleum ether in the proportion of 2:1 and the following crops of crystals were obtained as the result of an exhaustive fractional crystallization of the solution: (1) unchanged 1,3-benzylidene glycerol (m. p. 83°), yield 2 g.; (2) unchanged 1,3-benzylidene glycerol (m. p. 80°), yield 2 g.; (3) 1,3-benzylidene-glycerol-2-methyl ether,? (m. p. 51°), yield 9 g.; (4) unchanged 1,3-benzylidene glycerol (m. p. 78°), yield 0.5 g.; (5) a residual oil, weight 4.5 g. The residual oil was investigated for the presence of the isomeric 1,2-benzylidene glycerol and of its methyl ether, but with negative results. The original 1,3-benzylidene glycerol apparently undergoes extensive hydrolysis to glycerol and benzaldehyde under these conditions.

p-**Nitrobenzoylation** of the Oil Obtained in the Previous Experiment.—Four and one-half grams of Fraction V (the above residual oil) was added with shaking to 4.5 g. of p-nitrobenzoyl chloride dissolved in 19.8 g. of pyridine. After standing overnight at 20°, the mixture was poured into 400 cc. of water, the precipitate which formed filtered off and dissolved in benzene–petroleum ether (2:1). The crystals which separated on cooling were recrystallized from ethyl acetate and then had a melting point of 153–154° (melting point of 1,3-benzylidene glycerol-2-p-nitrobenzoate, 156°).[7] Four successive crops of crystals were obtained from the mother liquor, all having a melting point of 153–154°. Ligroin (30–50°) was then added to the mother liquor until the solution became murky. On cooling a last crop of crystals was obtained with a melting point of 152°. 1,2-Benzylidene-glycerol-3-*p*-nitrobenzoate, which would have been present had ring shift occurred during methylation, melts at 91°.[7] There was thus no evidence of any ring change.[9]

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[9] The evidence submitted in this and the preceding paper renders it highly improbable that any "ring shift" or "wandering of a methyl group" occurs during the methylation of glucosides, anhydro sugars and polysaccharides, except in the isolated cases where the product in question undergoes ready hydrolysis by water, thus involving ring scission.

On the other hand, abnormal results are to be expected in the methylation of the free sugars in alkaline solution, since in these cases (that is, where a free carbonyl group is present) there is the possibility of a "Lobry de Bruyn–van Ekenstein transformation" involving conversion of the sugar into an equilibrium mixture of different carbohydrates or polyoses.

That other deep-seated changes are involved is indicated by the decrease in the rotation of a 0.25 M glucose solution to practically zero, in twelve hours, under the influence of 0.85 N potassium hydroxide [J. Groot, *Biochem.* Z., 146, 72 (1924)].

The low yield of β-methyl glucoside when prepared by the action of dimethyl

Summary

1. Methylation of 1,3-benzylidene glycerol, using dimethyl sulfate and sodium hydroxide under acid and alkaline conditions, has been described.

2. Attention has been drawn to the difficulty of methylating the 1,3-benzylidene glycerol under non-alkaline conditions. In the presence of an excess of dimethyl sulfate (that is, in an acid medium), 1,3-benzylidene glycerol undergoes ring scission into benzaldehyde and glycerol. It was not found possible to isolate any monomethyl ether of either the five- or the six-membered ring isomers.

3. Under alkaline conditions methylation takes place more readily, with formation of the corresponding methyl ether. The methylation is not accompanied by ring migration, as is evidenced by the absence of any 1,2-benzylidene-glycerol-3-methylether, although extensive hydrolysis occurs.

4. The necessity for great care in drawing conclusions from methylation experiments carried out on cyclic acetals, carbohydrates and polysaccharides in acid media is pointed out.

MONTREAL, CANADA

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sulfate and sodium hydroxide on glucose [Maquenne, *Bull. soc. chim.*, [3] 33, 260, 469 (1925); Schlubach and Maurer, *Ber.*, 57, 1686 (1924)] would also seem to indicate the existence of other reactions in an alkaline medium.

For these reasons there would seem to be some doubt as to the presence of a new "active or gamma-sugar" formed under the conditions indicated in the recent paper of Whitnah [THIS JOURNAL, 51, 3490 (1929)].

It is, however, to be expected that the nature of the glucoside formed in *neutral* and very *slightly* acid solutions of carbohydrates such as glucose, will vary markedly both with regard to the number and type of ring isomers formed, in accordance with the PH value of the medium used. This has been pointed out repeatedly by the senior author in the last few years and is now found to be the case experimentally. The results are to be published in the near future and the reservation of this field (glucoside formation in neutral and faintly acid media) in view of long years of previous preparation is courteously requested for a short period. [H. H.]

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

PREPARATION, PROPERTIES AND REACTIONS OF LEAD MERCAPTIDES[1]

P. BORGSTROM,[2] L. M. ELLIS, JR.,[3] AND E. EMMET REID[4]

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Lead mercaptides have been known for a long time and have been used primarily for the removal of mercaptans from solution or in synthetic work for the introduction of the mercapto group. In the last few years the petroleum industry has also become interested in the properties of the lead mercaptides in connection with the "sweetening" of petroleum by the use of sodium plumbite.[5] In studying the properties of these mercaptides, there is a lack of information on the purity and solubility. In this paper certain lead mercaptides will be discussed as to methods of preparation, their analyses, solubility and some reactions.

TABLE I

PREPARATION AND ANALYSES OF LEAD MERCAPTIDES

Mercaptan	Percentage of lead Calculated	Found	Preparation
Ethyl	62.92	62.84, 62.89	Recrystd. from EtOH
n-Propyl	58.02	57.66, 58.41	Washed thoroughly, vacuum dried
Isopropyl	58.02	57.99, 57.98	Washed thoroughly, vacuum dried
n-Butyl	53.79	53.41, 53.35, 53.36	Recrystd. from *n*-BuOH or EtOH
Isobutyl	53.79	54.03, 54.26	Recrystd. from EtOH
Iso-amyl	50.10	50.13, 50.42	Recrystd. from MeOH
Benzyl	45.72	45.55, 45.55	Washed and vacuum dried
Thiophenol	48.70	48.72, 48.96	Washed and vacuum dried
y-Hydroxypropyl	53.21	53.13, 53.15	Recrystd. from 50% EtOH

Experimental

Preparation of Lead Mercaptides.—The desired mercaptan dissolved in 6 to 10 parts of ethyl alcohol was added to a warm 50% alcoholic solution of $M/4$ lead acetate until a cloudiness appeared. It was then heated to boiling (more alcohol added if necessary to obtain a clear solution), allowed to cool and crystallize. The crystals were washed several times by decantation, then thoroughly on the filter and finally dried in a vacuum desiccator. Whether it is desirable to recrystallize is questionable, for the analyses given in Table I of different mercaptides show no improvement in purity for the recrystallized samples. Recrystallization may even be detrimental, for unrecrys-

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[1] This paper contains results obtained in an investigation on "A Study of the Reactions of a Number of Selected Organic Sulfur Compounds," listed as Project No. 28 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] American Petroleum Institute Research Associate.

[3] American Petroleum Institute Research Assistant.

[4] Director of Project No. 28.

[5] W. A. Gruse, "Petroleum and Its Products," McGraw-Hill Book Co., New York,

tallized n-propyl, isopropyl and thiophenol mercaptides were more stable than iso-amyl, benzyl arid γ-hydroxypropyl which were recrystallized. If, in preparation of the mercaptides, the concentration of lead acetate and mercaptan was too great, the lead mercaptide often separated as an oil which solidified on cooling. This occurred with n-butyl and iso-amyl. n-Butyl mercaptide can be recrystallized from n-butyl alcohol as well as ethyl alcohol, but if the oil or crystals became slightly superheated, immediate darkening occurred and decomposition began. This happened with the n-butyl readily. *Iso*-amyl mercaptan in oily form was slightly soluble in acetone, n-butyl alcohol, ethyl alcohol and methyl alcohol. It was finally recrystallized from methyl alcohol, which was a slow process due to low solubilities. The lower mercaptides, that is, ethyl, n-propyl and isopropyl separated very readily in the crystalline form when prepared and therefore were analyzed as prepared.

To obtain lead mercaptides that have a constant melting point on recrystallization was impossible. On recrystallizing there probably is a slight decomposition due to reaction with the alcohol and this slight impurity may be the cause of the indefinite values found. For instance, one sample of ethyl lead mercaptide recrystallized from *95%* ethyl alcohol coalesced at 119° and blackened at 124° and on an attempted second recrystallization had undergone decomposition and did not melt up to 170°. *A* second sample of this coalesced at 104°, and pronounced change occurred at 110° turning deep red. Another sample dried in *vacuo* for twenty-four hours darkened at 110–112°.[6] With n-propyl lead mercaptide the usual temperature at which a first change appeared was 89–90° when softening occurred; it melted at about *9496";* but even this was not at all satisfactory. Isobutyl mercaptide changed to a wax-like substance at *66°* and melted at *71°*. On recrystallization it became wax-like at *60–61"* and was not completely molten at 130°. Benzyl mercaptide began to coalesce at 98° and decomposed without melting at *100–101°*.

An attempt was made to determine qualitatively the solubility of the lead mercaptides after they had been once recrystallized, washed and thoroughly dried in a vacuum desiccator. Ethyl mercaptide recrystallized from ethyl alcohol and n-butyl mercaptides recrystallized from n-butyl alcohol were used as samples with carbon tetrachloride; both turned dark within twenty-four hours. With acetone (C. P.) the mercaptide became white. With ethyl alcohol there was a change similar to that with acetone but not as marked. With n-butyl alcohol there was some solubility, for when the solutions were heated to 50° and then cooled again crystals of the yellow mercaptide separated. This was especially true for n-butyl lead mercaptide. With a carefully purified low-boiling hydrocarbon there was practically no solubility, as the naphtha was colorless and on evaporating *25* cc. no stain was found in the beaker. There was no visible decomposition in the same time in which decomposition appeared with carbon tetrachloride. Using C. P. benzene freshly distilled from sodium there was no visible decomposition.

Reactions.—To *C.P.* benzene freshly distilled from metallic sodium, and the recrystallized mercaptides, in *50-cc.* sample bottles, small amounts of C. p. sulfur (powdered) were added. With ethyl mercaptide there was an immediate darkening, sometimes first brown and then to black. With benzyl and n-amyl there was the same darkening. With n-butyl it became red first and then dark. The reaction was very rapid. Using the same benzene and mercaptides and adding some of this same benzene saturated with dry hydrogen sulfide there appeared immediately a brown to black color with ethyl, n-amyl and benzyl. With n-butyl a reddish color first appeared at first, which then changed to brown and finally black. This color play has been noted with the "doctor"

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[6] R. Otto, *Ber.*, 13, 1290 (1880), gives the melting point for lead ethyl mercaptide as 150°.

solution and naphthas using sodium plumbite and sulfur.[7] Whether the color play in both cases is due to the same original compound is not proved by these experiments.

An attempt was made to use the titration with iodine in benzene represented by the equation $Pb(SR)_2 + I_2 \longrightarrow PbI_2 + (SR)_2$ as an analytical method, but this was not very successful. The reaction was rapid at first, slow after half of the iodine had been absorbed, and toward the end very slow. The benzene used was freshly distilled from sodium. The lead iodide formed was filtered into a Gooch crucible, washed, dried and weighed. The results are given in Table II.

TABLE II

RESULTS OF ANALYSES

		Mg. of iodine			PbI_2		
$Pb(SR)_2$	G.	Calcd.	Abs.	%	Calcd.	G.	%
Ethyl	0.3664	282.4	272.2	96.39	0.5129	0.5058	98.61
n-Amyl	.2558	157.1	154.5	98.34	.2854	.2750	96.36
Benzyl	.3788	212.1	178.5	84.16	.3853	.3500	90.83

Summary

Lead mercaptides have been prepared and analyzed and some of their properties noted.

BALTIMORE, MARYLAND

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

THE REACTION OF PHTHALYL CHLORIDE WITH AMIDES

BY THEODORE W. EVANS AND WILLIAM M. DEHN

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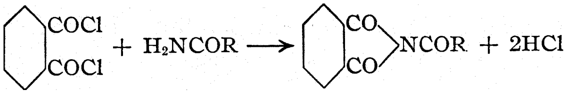
Acetylphthalimide[1] and benzoylphthalimide[2] are the only examples of substitution of the imino hydrogen of phthalimide by acid radicals. The acetyl derivative was prepared by the action of acetic anhydride on phthalimide, also by dehydration of acetylphthalamic acid; the benzoyl derivative was prepared by the action of benzoyl chloride on phthalimide in pyridine solution, also by dehydration of benzoylphthalamic acid.

Because compounds of this type were required in another study, we have investigated different methods for their preparation, and have found that phthalyl chloride reacts normally with amides



giving good yields[3] which were free from other products, especially such as

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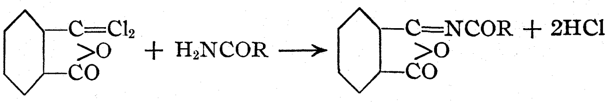
[7] G. L. Wendt and S. H. Diggs, *Ind. Eng. Chem.*, **16**, 1113 (1924); A. E. Wood, A. Lowy and W. F. Faragher, *ibid.*, **16**, 1116 (1924).

[1] Aschan, *Ber.*, **19**, 1400 (1885).

[2] Titherley and Hicks, *J. Chem. Soc.*, **89**, 708 (1906). For a general discussion of methods of acylation of amides, see Titherley, *ibid.*, **85**, 1679 (1904).

[3] Titherly concluded that the action of an acyl chloride on amides is "a poor method, applicable only to the primary amides of the aliphatic series."

might be expected if the isomeric form of phthalyl chloride reacts in accordance with the equation



When equivalents of the phthalyl chloride and the amide were heated, either without a solvent or in toluene until no more hydrogen chloride was evolved, the products could be purified by one crystallization. This method was invariably successful but other methods failed.

For example, p-tolylsulfonylphthalimide was easily prepared by this method, but could not be prepared by any of the following methods: heating phthalic anhydride and p-toluenesulfonamide, heating potassium phthalimide with p-toluenesulfonyl chloride or heating phthalimide with p-toluenesulfonyl chloride in pyridine. Also, heating benzenesulfonamide and phthalic acid to 230° failed to give benzenesulfonylphthalimide, easily obtainable from phthalyl chloride and benzenesulfonamide.

TABLE I

PREPARATIONAL DATA

Crystallized from Toluene

Amide used	Formula A = $C_8H_4O_2N$	Crystal form	M. p., °C.	Calcd. S	Found, S
Acetamide	$ACOCH_3$	Octahedra	135–136	...	...
Benzamide	$ACOC_6H_5$	Prisms	168	...	...
Benzene sulfon-	$ASO_2C_6H_5$	Needles	205	11.12	10.62
o-Tolyl sulfon-	$ASO_2C_6H_4CH_3$	Prisms	182	10.59	10.39
p-Tolyl sulfon-	$ASO_2C_6H_4CH_3$	Prisms	231	10.59	10.36
p-Tolyl-m-nitro-sulfon-	$ASO_2C_6H_3CH_3NO_2$	Needles	247	9.26	8.95
Urea[a]	$\overline{C_6H_4CONHCONHCO}$	Needles	188–190	...	...
2,5-Dichloro-aniline	$AC_6H_3Cl_2$[b]	Hair-like Needles	185–190	Cl, 24.28	Cl, 24.68

[a] Piutti, *Ann.*, 214, 23 (1882), prepared this compound from phthaluric acid.

[b] Crystallized from benzene.

Summary

The imino hydrogen of phthalimide is readily substituted by acid radicals when phthalyl chloride reacts with amides.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

PARA-BROMOPHENYL-4-SEMICARBAZIDE[1]

BY ALVIN S. WHEELER

RECEIVED AUGUST 3, 1929 PUBLISHED DECEMBER 11, 1929

This paper is a continuation of studies[2] in this Laboratory on semi. carbazides as ketone reagents. *p*-Bromophenylurea, from which the semicarbazide was prepared, has not been satisfactorily characterized. We prepared it by three different methods: **(1)** by the action of bromine on phenylurea in glacial acetic acid solution;[3] (2) by the action of bromine on an alcoholic solution of phenylurea; **(3)** by the action of potassium cyanate on p-bromo-aniline hydrochloride in hot water solution. Each method has its advantages. The impure product behaved so erratically on heating that much time was lost in arriving at a pure product. If heated rapidly, it melts; if slowly, it does not melt, In either case it decomposes at an elevated temperature. The statement of Pinnow that it decomposes at about 260° evidently is incorrect.

The semicarbazide was prepared according to the method of Curtius[4] and Burkhardt, who prepared phenylsemicarbazide. p-Bromophenylurea was heated for fifty hours with an excess of hydrazine hydrate. The pure product melts at **252** and at 254° decomposes to a claret-colored liquid.

Semicarbazones were obtained by treating alcoholic solutions of the semicarbazide with the following ketones: acetone, methyl ethyl ketone monochloro-acetone, *α*,y-dichloro-acetone, acetophenone and benzophenone.

Experimental

p-Bromophenylurea, $C_6H_4BrNHCONH_2$.—This compound was first made by Pinnow.[3] He treated a glacial acetic acid solution of phenylurea with bromine. Two of the workers in this research (Pritchard and Andrews) preferred an alcoholic solution, while the others preferred a very different method, *i. e.*, the action of potassium cyanate on *p*-bromo-aniline hydrochloride in hot water. The product may be purified by hot water (soluble in 200 parts); hot alcohol (soluble in 7 parts); glacial acetic acid (soluble in 5 parts) or from benzene If alcohol or acetic acid is used, the solution is poured into cold water. It crystallizes in long colorless needles which behave peculiarly on heating. If the rate of heating is 50° per minute or faster, the substance melts at 220°, resolidifies about 225° and decomposes at about 296" to a black rubber-like substance. When heated slowly no apparent change occurs until decomposition takes place at 296°. Pinnow states that decomposition without melting occurs at 260°.

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[1] This research was begun by Paul R. Bryan, continued by W. N. Pritchard, Jr., T. M. Andrews and J. A. Bender, and completed by J. G. Park.

[2] Wheeler and Bost, THIS JOURNAL, 46, 2813 (1924); Wheeler and Walker, *ibid.*, 47, 2792 (1925); Wheeler and Norton, *ibid.*, 50, 2488 (1928); Wheeler and Park, *ibid.*, 51,3079 (1929).

[3] Pinnow, Ber., 24, 4172 (1891).

[4] Curtius and Burkhardt, J. prakt. *Chem.*, 58,205 (1898).

We have never observed any such behavior of the many preparations which we have made.

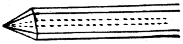
Anal. Calcd. for $C_7H_7ON_2Br$: Br, 37.20. Found: (Paul R. Bryan) 37.23; (W. N. Pritchard, Jr.) 37.37.

p-Bromophenyl-4-semicarbazide, $C_6H_4BrNHCONHNH_2$.—The semicarbazide was prepared by boiling an absolute alcoholic solution of bromophenylurea with hydrazine hydrate. Many variations of proportions of materials were tried. The time of boiling was also varied. The best yield was obtained by J. G. Park: 5.4 g. of bromophenylurea, 30 cc. of absolute alcohol and 7.5 g. of 42% hydrazine hydrate (2.5 equivalents) were boiled under a reflux condenser for fifty hours. After determining that an excess of hydrazine hydrate was necessary, it was found that prolonging the time of heating increased the yield. A gradually diminishing undissolved portion remained for eighteen hours, complete solution then occurring. The product was finally poured into a beaker, evaporated to one-half of its original volume and cooled. Dense crystallization took place. Water was added to effect complete separation and the yield of the crude product was 4.8 g. It was purified by adding it to 20 cc. of alcohol and 20 cc. of concd. hydrochloric acid and boiling. It was then cooled and the precipitate filtered off. Any unchanged phenylmea was isolated by boiling the product with 200 cc. of water to extract the semicarbazide hydrochloride. The insoluble bromophenylurea was filtered off and the semicarbazide in the filtrate precipitated by adding caustic potash solution. One gram of bromophenylurea was recovered. Bromophenylsemicarbazide crystallizes in small needles from hot alcohol. It is insoluble in cold water and cold alcohol. It decomposes with effervescence at 254° to a claret-colored liquid.

Anal. Calcd. for $C_7H_8ON_3Br$: Br, 34.78. Found: (Pritchard) 35.12.

Semicarbazones

p-Bromophenyl-4-semicarbazone of Acetone, $C_6H_4BrNHCONHN(CH_3)_3$.—0.25 g. of the semicarbazide was dissolved in 15 cc. of hot alcohol and an excess of acetone added. The mixture was boiled for twelve hours. Upon cooling the solution very beautiful prismatic crystals separated. The crystals had three wide faces and three narrow ones and the ends formed pyramids.



The product melts sharply at 174° (corr.) to a colorless liquid. It is insoluble in cold water or cold alcohol but dissolves in hot alcohol.

Anal. Calcd. for $C_{10}H_{12}ON_3Br$: Br, 29.62. Found: (Pritchard) 29.40.

TABLE I

SEMICARBAZONES

	Ketone	Crystal form	M. P.,[a] °C.	Time of heating
1	Methyl ethyl ketone	Rect. plates	175	1 Hour
2	Chloro-acetone	Needles	182 dec.	5 Min.
3	α,γ-Dichloro-acetone	Needles	196 dec.	5 Min
4	Acetophenone	Bulky needles	218	5 Hours
5	Benzophenone	Bulky needles	205	10 Hours

[a] All temperatures are corrected except that for acetophenone.

	Formula	Bromine, % Calcd.	Bromine, % Found
1	$C_{11}H_{14}ON_3$	28.14	27.98
2	$C_{10}H_{11}ON_3ClBr$	26.24	25.90
3	$C_{10}H_{10}ON_3Cl_2Br$	23.58	23.68
4	$C_{15}H_{14}ON_3Br$	24.07	24.00
5	$C_{20}H_{16}ON_3Br$	20.28	20.15

This reaction was also carried out in the cold, using a vacuum to concentrate the solution.

Other semicarbazones are indicated in Table I. All were prepared by J. G. Park except No. 4, which was prepared by W. N. Pritchard, Jr. In all cases the reacting compounds were dissolved in alcohol and the products were recrystallized from alcohol.

Summary

The preparation of *p*-bromophenylurea by three methods is described and procedure is given for its conversion into *p*-bromophenyl-4-semicarbazide. The usefulness of the semicarbazide as a ketone reagent has been tested by the preparation of several semicarbazones.

CHAPEL HILL, NORTH CAROLINA

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

IV. THE CHEMICAL EFFECTS OF ELECTRICAL DISCHARGE IN BUTANE. FRACTIONATION OF THE LIQUID PRODUCT[1]

BY S. C. LIND[2] AND GEORGE GLOCKLER[3]

RECEIVED AUGUST 5, 1929 PUBLISHED DECEMBER 11, 1929

Introduction

In a former paper[4] it was shown that butane, as well as other hydrocarbons, yields liquid condensates when subjected to the semi-corona electrical discharge. At the same time, however, it was found that solid condensation products are also formed on the inner walls of the discharge tubes. From previous experience it was known that this solid formation does not occur in an all-glass ozonizer, or at least that such action is very slow.

Since the *object of the present work was the production of a fairly large amount of liquid condensate from butane gas by electrical means and its fractional distillation,* it was decided to build an all-glass ozonizer apparatus consisting of twelve ozonizers connected in parallel as to gas flow and as to electrical wiring. This apparatus is shown in Fig. 1. It may be said at once that indeed the solid formation just mentioned was quite negligible and only near the upper ends of the ozonizers toward the close of the long experiment was there any solid product formed.

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[1] This paper includes part of an investigation of "The Effect of Electrical Discharge upon Gaseous Hydrocarbons," Project No. 8 of American Petroleum Institute research. Financial assistance has been received from the research fund of the American Petroleum Institute, donated by the Universal Oil Products Company. This fund is administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project No. 8.

[3] American Petroleum Institute Research Associate.

[4] Lind and Glockler, THIS JOURNAL, 51, 2811–22 (1929).

Experimental Procedure

The ozonizers were supplied with about 20,000 volts from the secondary of a Thordarson transformer using a primary current of about 12 amperes and a primary voltage of about 110 volts. During the initial stages of the experiment the machine was kept in operation during the daytime only, in order to study its behavior. On account of the possibility of breakdowns and fires resulting therefrom it was necessary to watch the apparatus and when the run was finally made continuous during the twenty-four hours of a day it was necessary to have a watch maintained at all times. The apparatus was run for 659.2 hours at a gas flow of 3.46 liters of butane (25°, 1 atm.) per hour. There were then used 5420 g. of butane which yielded 1041 cc. of liquid condensate weighing 832.8 g., having a density of 0.804. These figures show that 15.37% by weight of the butane used was converted into liquid condensate. The temperature of the apparatus was about 50° due to the electrical energy consumed (356 k. w. h.), since the twelve ozonizers were protected by asbestos boards (not shown in Fig. 1). This higher temperature was found to aid the run-off of the liquid condensate as previously noted.[5] The performance of the apparatus was followed by noting daily the amount, color and index of refraction of the liquid product. Its average index of refraction was 1.4600 and its average molecular weight in benzene by the freezing-point method was found to be 178. The color on the arbitrary scale of the Union Oil Co. colorimeter was about 2.75 scale readings. The exit gases have not been analyzed since the primary interest in this present research was concerned with the production and fractionation of the liquid condensate.

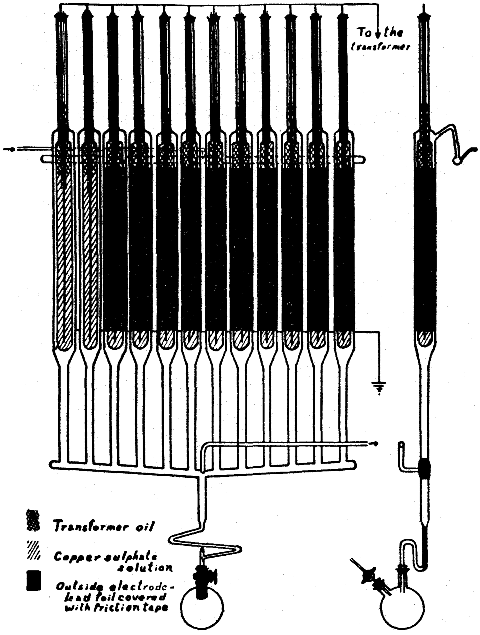


Fig. 1.—Twelve ozonizer tubes in parallel.

Fractionation of the Liquid Condensate.—In order to carry out the fractional distillation of the liquid hydrocarbons obtained from butane, a small chain-still[6] was built having an 18-inch column filled with iron chain (about $^1/_8$-inch link). With this still the liter of liquid product was distilled at low pressure (using liquid–air traps to avoid loss) and was separated into three main fractions, as shown in Table I.

The Middle Fraction 11.—The fractions noted in Table I are still complex mixtures of liquid hydrocarbons and they were in turn subjected

[5] Lind and Glockler, THIS JOURNAL, 50, 1767 (1928).

This still was built after a drawing obtained from Dr. E. W. Washburn, Bureau of Standards, Washington, D. C. We wish to thank Dr. Washburn for much valuable information regarding distillation problems which was obtained from him during a visit at the Bureau.

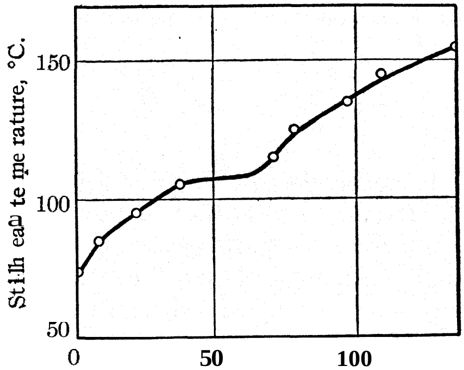
TABLE I

EXPERIMENTAL DATA

No	Fraction	Vol., cc.	Density	Wt. g.	B. p., range °C.	B. p., range mm.	Index of refraction
I	Light (liq.-air trap)	450	0.740	335	0–160	740	1.3713–1.4334
II	Middle (cond. at room temp.)	117	.795	93	78–112	5	1.4386–1.4558
III	Heavy (rem. as residue)	465	.872	405	230	10^{-4}	1.4855
		1032	0.804	833			

to further fractional distillation. The middle fraction (II) was thus separated (at 5-mm. pressure) into five sub-fractions boiling between 90 and 98° with a large residue of 38 g. These sub-fractions were again distilled at low pressure in a smaller still of the same design into 14 further small fractions. The range of boiling points now widened to 78–112°. The amounts of the fractions were now rather small and further attempts of separating "middle fraction II" will be made at a later date when more of this material is available for investigation.

The Heavy Fraction III.—This material is the residue which remained in the distilling flask. It is very viscous and has an index of refraction of 1.4855. Beyond the fact that the material is a mixture nothing has been found out about it. It was possible to distil from this heavy oil a much lighter yellow oil at about 230°, using a Nickel-Shot Bath and a very low pressure (10^{-4} mm.). It is hoped to study this heavy fraction in greater detail later.



Grams of distillate (light fraction I).

Fig. 2.

The Light Fraction, I.—This low-boiling section is the material caught in the liquid-air trap and contains, of course, a great deal of dissolved butane. This gas was removed and collected and its boiling point determined. The total amount of butane (147 g.) was distilled at 0° with exception of a few cubic centimeters which remained as a residue and which must represent slightly higher hydrocarbons. The next material that came over on distilling the "light fraction I" was separated into eleven sub-fractions by making cuts every 10°. The details of this fractionation are shown in Table II; Fig. 2 gives the distillation curve.

It is seen that Fraction I-6 is the largest fraction boiling within a ten-degree interval. This fraction was, therefore, redistilled into five sub-sub-fractions boiling between 105 and 117°.

TABLE II

FRACTIONATION OF THE "LIGHT FRACTION I" INTO ELEVEN SUB-FRACTIONS (BAROMETER 740 MM.)

No.	Temp. of still-head, °C.	n^{20}_{sun}	Distillate in grams Each fraction	Total
I-1	26.5–68.0	1.3713	0.2	0.2
I-2	68.0–80.0	1.3843	0.3	0.5
I-3	80.0–90.0	1.3904	7.5	8.0
I-4	90.0–100.0	1.3938	13.5	21.5
I-5	100.0–110.0	1.3997	16.5	38.0
I-6	110.0–120.0	1.4003	33.0	71.0
I-7	120.0–130.0	1.4058	7.5	78.5
I-8	130.0–140.0	1.4110	18.5	97.0
I-9	140.0–150.0	1.4160	12.0	109.0
I-10	150.0–160.0	1.4204	26.0	135.0
I-11	160.0–	1.4334	53.0	188.0
			188.0	

TABLE III

FRACTIONATION OF SUB-FRACTION I-6 INTO FIVE SUB-SUB-FRACTIONS (BAROMETER, 744.2 MM.)

No.	Temp. of still-head, °C.		Distillate, g.
I-6-1	105.0–110.0	1.4004	0.5
I-6-2	110.0–113.0	1.4021	8.0
I-6-3	113.0–115.0	1.4029	6.0
I-6-4	115.0–117.0	1.4036	2.0
I-6-5	117.0–	1.4118	10.0
			26.5

Identification of Fraction I-6-2.—On comparing the boiling point of this fraction and its index of refraction with known hydrocarbons (I. C. T.), it was found that two octanes fit closest in these two properties. They are 2,4-dimethylhexane and 2-methyl-3-ethylpentane. Several properties of this unknown hydrocarbon were therefore determined, such as density, carbon–hydrogen ratio, molecular weight by the freezing-point method in benzene and halogenation number. At the same time these methods were checked on a sample of pure heptane available in the laboratory.

The properties are given in Table IV. The freezing-point determination was checked with pure naphthalene; the combustions were carried out with 0.200-g. samples in an enclosed system;[7] the halogenations were performed by the iodine-bromide-in-CCl_4 method[8] and checked against cyclohexene and cymene.[9]

It is at once seen that the unknown material I-6-2 is not a system of

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[7] Geo. Glockler and L. D. Roberts, THIS JOURNAL, 50, 828–31 (1928).

[8] E. M. Johansen, *J. Ind. Eng. Chem.*, 14, 288 (1922).

[9] The iodine number of cyclohexene was found to be 304 (calcd. 310). By another method Faragher, Gruse and Garner, *J. Ind. Eng. Chem.*, **13**, 1044 (1921), found 298. Cymene was also studied and no addition was found, while substitution takes place at a slow rate.

TABLE IV

PROPERTIES OF PURE HEPTANE, THE UNKNOWN HYDROCARBON I-6-2 AND TWO KNOWN OCTANES

Property	Heptane "I. C. T."	Heptane Oba	Octanes: 2,4-Dimethylhexane and 2-methyl 3-ethylpentane ("I. C. T.")	Octanes: Unknown I-6-2
Boiling point, °C.	98.0	97-98	110.0-114.0	110.0-113.0
Density	0.684	0.681	0.708	0.708
Index of refr.	1.3850	1.3855	1.4016-26	1.4021
Carbon, %	83.90	83.79	84.11	84.55
Hydrogen, %	16.10	16.21	15.89	15.45
Mol. wt. freezing point	100.12	102.0	114.1	114.7
Mol. wt. combustion	..	..	....	113.5
Mol. wt. halogenation	..	..	....	113.7
Empirical formula by combustion	C_7H_{16}	...	C_8H_{18}	$C_8H_{17.4}$
Unsaturation combustion, %	..	..	..	30.0
Unsaturation halogenation, %	..	..	..	22.5

saturated octanes but the halogenation and combustion data show the presence of unsaturated substances. Since the molecular weight, density and index of refraction are very closely those of octanes, it may be assumed that the unsaturation found is due to octylenes.

Discussion of Results.—It is believed that in this work the largest quantity of liquid condensate ever produced from a gaseous hydrocarbon by electrical means has been made. Furthermore, the fractional distillation of this material has been carried to a more detailed extent than has been accomplished by previous investigators. For instance, Pryanishnikow[10] has studied the liquid condensation products obtained from ethylene by electrical discharge, but his fractionation involves cuts covering much larger temperature intervals than is the case in the work reported here. Of course, the identification presented here has therefore a better basis. It would require a still larger amount of liquid condensate to push the separation still further. This would involve the identification of isomeric octanes and octylenes and this problem has not been solved completely even with ordinary hydrocarbon materials.

The distillation curve of the "light fraction I" (Fig. 2) shows that the Fraction I-6 (33 g.) is the largest fraction obtained. From the range of boiling points of this fraction obtained upon further fractionation and from the detailed study of Sub-Fraction I-6-2 it appears that these materials are octanes. Octanes or at least 8-carbon atom materials of molecular weights near octanes are then relatively most abundant in this final liquid product. This result seems to follow quite simply from the cluster theory of ionic gas reactions as proposed by one of us.[11] On this theory the reactions leading to condensation by doubling are as follows.

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[10] D. N, Pryanishnikow, Ber., 61B, 1358-1363 (1928).

[11] S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., Inc., New York, 2d ed., 1928, p. 100.

$$C_4H_{10} \longrightarrow C_4H_{10}^+ + E^- \text{ (Ionization)}$$
$$C_4H_{10}^+ + C_4H_{10} \longrightarrow (C_4H_{10}\cdot C_4H_{10})^+ \text{ (Clustering)}$$
$$(C_4H_{10}\cdot C_4H_{10})^+ + E^- \longrightarrow C_8H_{18} + H_2 \text{ (Neutralization of cluster and rearrangement of bonds)}$$

Since any butane ions formed would meet with neutral butane molecules most frequently because of the greater concentration of butane, it is to be expected that octanes would be formed relatively in greatest amount. Of course, other possible hydrocarbons would be built by continued and successive actions of the type referred to and since decomposition would also take place it is readily understood that probably all possible combinations of radicals take place in such a manner as to produce a most complex mixture of hydrocarbons.

Just which of the isomeric octanes would be produced in greatest amount would depend upon the reactivity of the various carbon–hydrogen bonds of the butane molecule, and, since it has not been possible to identify the isomers of octane formed, this question must await further experimentation. The octylenes found can be thought to be formed by splitting off two hydrogen molecules upon reaction and rearrangement as typified in Equation **3** above.

In future work it is hoped to carry on the study and identification of some of the other larger fractions as obtained from the present series of distillations and to produce still greater quantities of the original mixture for a more detailed fractionation.

The authors wish to thank Mr. J. L. Wilson, who has assisted in this work as American Petroleum Institute Research Assistant.

Summary

A quantity of liquid hydrocarbons (1041 cc.) has been prepared from gaseous butane by condensation in an electrical discharge. A system of twelve all-glass ozonizers was used for the purpose. The liquid product obtained was separated into 40 fractions by fractional distillation at various pressures. These fractions consist of very light, medium and also very viscous oils. One of the light fractions was studied in detail and found to have the following properties: b. p. 110–114.0°; index of refraction, 1.4021; density, 0.708; molecular weight, 114.7; percentage of carbon, 84.55; percentage of hydrogen, 15.45; empirical formula, $C_8H_{17.4}$; unsaturation by halogenation, 22.5 mole per cent. These properties serve to identify this material as a mixture of octanes and octylenes. It is interesting to note that this largest fraction of the lighter oils consists of eight-carbon-atom molecules which can be produced from butane by simple doubling according to theory.

MINNEAPOLIS, MINNESOTA

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

DERIVATIVES FOR THE IDENTIFICATION OF MERCAPTANS[1]

BY E. WERTHEIM

RECEIVED AUGUST 6, 1929 PUBLISHED DECEMBER 11, 1929

For the identification of mercaptans the preparation of lead or mercury salts has been recommended in the literature. These are reported to be easy of preparation and purification and to have definite melting points. Reid[2] has advocated the use of 1.5-butyl-anthraquinone-sulfone sodium sulfonate. Prom this compound he has prepared derivatives of mercaptans having high and sharp melting points. So far as the writer is aware this compound is not on the market and would need to be prepared for individual use.

On account of the growing importance and availability of the mercaptans, it seemed of interest to review the subject of their identification and to fill the gaps in the literature regarding mercaptans now available.

The literature reports of lead and mercury salts are very scanty; the inference is that all of them have not been prepared. In this work the salts were made by adding 6 drops of the mercaptan to about 2 cc. of ethanol, subsequently adding an excess of lead acetate solution (20%) or mercuric cyanide solution (10%). After shaking and cooling the mixture for a few minutes the resulting precipitates were separated by filtration and dried in the air for a short time on a porous plate. They were purified by one recrystallization from the appropriate solvent, The mercury salts were crystallized from ethanol. The solvents used for the lead salts are shown in the following table. The melting points of the lead and mercury salts are given in Table I. The values shown in parentheses were obtained from the literature.

TABLE I

MELTING POINTS OF LEAD AND MERCURY SALTS OF MERCAPTANS

Alkyl	Lead salt, °C.	Mercury salt, °C.
Methyl	. . .	(175)
Ethyl	(150°)	(76)
Propyl	. . .	(68) 71–72
Isopropyl	91–92[a]	62-63
Butyl	80–81[b]	85–86
Isobutyl	. . .	94–95
Amyl	. . .	74–75
Iso-amyl	. . .	(100)
Heptyl	94–95[c]	76–77

[a] Solvent, ethanol. [b] Solvent, chloroform and ethanol. [c] Solvent, benzene.

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[1] This problem was originally assigned to C. H. Adams for a Master's thesis. However, owing to a combination of circumstances, he was unable to continue the work. I wish to thank Mr. Adams for the preparation of several of the compounds described.

[2] Reid, THIS JOURNAL, 45, 1837 (1923).

It will be noted that several of the lead salts are not reported. These precipitated as gummy masses which did not harden for some time and were deemed unsuitable for the purpose at hand. The melting points of the mercury compounds are seen to lie within a small range and several are practically identical.

In this work mercaptan derivatives were also prepared from 3,5-dinitrobenzoic acid and from 3-nitrophthalic anhydride, both of these compounds having proved of value for the identification of alcohols.

Preparation of Derivatives of **3,5-Dinitrobenzoic Acid.**—3,5-Dinitrobenzoyl chloride was prepared as directed by Mulliken[3] from 4 g. of 3,5-dinitrobenzoic acid and 5.5 g. of phosphorus pentachloride. Two grams (one mol) of the resulting acid chloride was placed in a test-tube with 1.5 mols of the mercaptan. The reaction was catalyzed by the addition of 4 drops of pyridine. The tube was then gently heated from time to time until the fumes of hydrogen chloride ceased to appear. In most instances the reaction was complete in about ten minutes; where this was not the case the tube was placed in hot water until the reaction had been completed.[4] A few drops of water were added to the mixture, then pyridine was added dropwise until the odor showed an excess of this reagent. Upon vigorous stirring the mass within the tube quickly solidified. It was brought upon a filter, washed with water and then placed upon a porous plate. One or two recrystallizations of the dried product from dilute alcohol or dilute acetic acid usually gave compounds of constant melting point.

On the small scale (for identifications) 0.2 g. of acid chloride, 6 drops of the mercaptan and 1 or 2 drops of pyridine were treated essentially as described above. For the preparation of the amyl and iso-amyl derivatives it was necessary to use an excess of the acid chloride.

The pure compounds are colorless or very faintly yellow and are odorless. They were made in lots of several grams as indicated above and analyzed

TABLE II

DERIVATIVES OF MERCAPTANS WITH 3,5-DINITROBENZOIC ACID

Alkyl	M. p., °C.	Analysis for sulfur Calcd.	Found	
Ethyl	61–62	12.50	12.57	
Propyl	51–52	11.85	11.60	
*Iso*propyl	83–84	11.85	11.74	
Butyl	48–49	11.27	11.14	
*Iso*butyl	63-64	11.27	11.25	10.92
Amyl	3940	10.74	10.31	10.76
Iso-amyl	4243	10.74	10.65	
Heptyl	52–53	9.82	9.85	
Phenyl[a]	148–149	10.52	10.27	
Benzyl[b]	119–120	10.06	10.08	

[a] M. p. of the benzoyl derivative is 56. [b] M. p. of the benzoyl derivative is 30.

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[3] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1911, Vol. I, p. 168.

[4] If the odor at this time proves the presence of a considerable excess of mercaptan, more of the acid chloride should be added and the heating continued. This may occur with the higher less volatile mercaptans.

in order to make sure that the reaction took the same course in each instance. The melting points and analytical data are given in Table II.

The melting points of the derivatives with 3,5-dinitrobenzoic acid are closer than would be desired and are, moreover, rather low.[5] Mixed melting points were taken for all compounds whose melting points lie within a few degrees of each other; a depression of melting point was observed in every such instance.

The use of 3-nitrophthalic anhydride for the identification of alcohols has been recommended by Nicolet and Sacks.[6] The compounds secured are especially convenient because they contain a free carboxyl group and may, accordingly, be titrated to secure the neutralization equivalent and thus the equivalent weight of the alkyl radical concerned.?

The derivatives of mercaptans and 3-nitrophthalic anhydride are exceptionally easy of preparation. The yields are good and these compounds may be recommended for the identification of mercaptans (excepting methyl mercaptan).

Preparation of Derivatives of Mercaptans with 3-Nitrophthalic **Anhydride.—**3-Nitrophthalic anhydride was prepared from the corresponding acid as directed by Nicolet and Bender.[8] Two grams (one mol) of the anhydride was treated in a test-tube with 1.5 mols of the mercaptan. After heating with a free flame for about one-half minute the tube was set aside. When cool about 20 drops of 10% sodium hydroxide solution was added in several portions. The tube was vigorously shaken between additions of the base and subsequently. It was cooled from time to time in an ice-bath if necessary. The mixture quickly assumed a plastic or oily consistency. About 10 drops of 5% hydrochloric acid solution was added and the tube again vigorously shaken. The solid was separated by filtration and dried on a porous plate. One or two recrystallizations from aqueous acetone or dilute acetic acid sufficed to give products of constant melting point.

For identifications 0.2 g. of the anhydride was treated with 6 drops of the mercaptan and approximately proportional amounts of sodium hydroxide and hydrochloric acid solutions. The products secured are colorless or very faint yellow; they are odorless. Analytical data and melting points are reported in Table III. The neutralization equivalents for several of these compounds were obtained and are also reported in the table.

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[5] It was to be predicted that these melting points would be lower than those of the known oxygen compounds. Part of the reason for their preparation was to see how much this difference would be.

[6] Nicolet and Sacks, THIS JOURNAL, 47,2348 (1925).

[7] McKenzie has shown (reference in Nicolet and Sacks' paper" that of the two possible mono-esters formed by the reaction of certain alcohols with 3-nitrophthalic anhydride, one is present in very small amount. Nicolet and Sacks' work indicates that this trace must be removed during the purification process. If in the reaction with mercaptans two mono-esters are produced it must again be true that one of them is lost during the purification, for the evidence given by the melting points of the compounds secured is that they are chemical individuals and not mixtures of isomers.

[8] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1927, Vol. VII, p. 74.

TABLE III

DERIVATIVES OF MERCAPTANS WITH 3-NITROPHTHALIC ANHYDRIDE

Alkyl	M. p., °C.	Analysis for sulfur Calcd.	Analysis for sulfur Found	Neutralization equiv. Calcd.	Neutralization equiv. Found
Ethyl	148–149	12.55	12.69	255	256.7
Propyl	136–137	11.82	11.19 11.76	269	267.3
*Iso*propyl	144–145	11.82	11.89	..	...
Butyl	143–144	11.31	11.17 11.12	...	...
*Iso*butyl	135–136	11.31	11.28 11.59	283	284
Amyl	131–132	10.77	10.64 10.50	297	297.4
Iso-amyl	144–145	10.77	10.62	297	298.5
Heptyl	131–132	9.84	9.91 9.88	325	326.2
Phenyl	130–131	10.56	10.56 10.36	...	...
Benzyl	136–137	10.09	10.22 10.04	317	318.8

The melting points given were secured when the bath was previously heated to about 100° and the temperature quickly raised to within about 10° of the true melting point. They are higher than those obtained when the compound is slowly heated from room temperature. The majority of the compounds show a slight decomposition at the melting point, liberating a gas. In identifications these compounds should be prepared from known samples of mercaptans, and the melting points of the known and unknown compounds should be taken together along with a mixed melting point.

Observation of the results given in the table will show that the melting points of these compounds again lie within a small range as Nicolet and Sacks noted for the oxygen compounds. Mixed melting points were taken for all pairs of compounds having melting points within a few degrees of each other. In every case a depression of the melting point was noted.

Summary

Derivatives of mercaptans have been prepared from lead and mercuric ions and from 3,5-dinitrobenzoic acid and 3-nitrophthalic anhydride. Their melting points and some other properties are reported. 3-Nitrophthalic anhydride is recommended for the identification of mercaptans (with the possible exception of methyl mercaptan, for whose identification the mercury salt appears to be preferable). Twenty-eight of the compounds reported are new.

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY AND BIOCHEMISTRY OF RUTGERS UNIVERSITY]

THE ACTION OF THIONYL CHLORIDE UPON CHOLESTEROL AND CERTAIN OTHER ALCOHOLS[1]

BY PAUL J. DAUGHENBAUGH AND JAMES B. ALLISON

RECEIVED AUGUST 9, 1929 PUBLISHED DECEMBER 11, 1929

Halogen derivatives of cholesterol, substituted monosaccharides and certain other alcohols were desired for further synthetic work. The isomerization, polymerization, reduced yields of the halide and sometimes destructive action which may result from the treatment of alcohols with the halogen derivatives of phosphorus has been pointed out by Darzens.[2] The reaction of diacetone-glucose with phosphorus pentachloride yielded 75% of compounds containing phosphorus.[3] Thionyl chloride acts as a milder reagent and does not cause the Walden inversion of certain optically active alcohols.[4] Darzens[2] offers a general method for the preparation of halogen derivatives of the aliphatic alcohols with good yields by the use of thionyl chloride or thionyl bromide in the presence of an organic base such as pyridine.

However, while attempting to prepare fenchyl chloride by the treatment of fenchyl alcohol with thionyl chloride in the presence of pyridine, Ruzicka and Liebl[5] obtained difenchyl sulfite. There was no chlorination. Richter[6] and Badische[7] have prepared a series of aryl sulfites in a similar manner. A study of the reaction indicated that an alcohol treated with the theoretical amount of thionyl chloride in the presence of pyridine would yield the organic ester of sulfurous acid. By this method the sulfurous acid esters of cholesterol, diacetone-glucose, ethyl alcohol, butyl alcohol and phenol have been prepared. There was no chlorination. These esters were also prepared by treating their sodium salts in petroleum ether or ethyl ether with the theoretical amount of thionyl chloride. This method was described in a previous paper for the preparation of *bis*-(diacetone-glucose)-sulfite.[3]

If a large excess of thionyl chloride is used on the alcohol in the presence of a small amount of pyridine, the reaction evidently goes according to Equation I. When refluxed, sulfur dioxide is eliminated according to Equation II.

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[1] The investigations upon which this article is based were supported by a grant from the firm of Johnson and Johnson of New Brunswick, N. J.

[2] Darzens, *Compt. rend.*, 152, 1314 (1911).

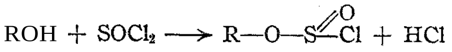
[3] Allison with Hixon, THIS JOURNAL, 48, 406 (1926).

[4] McKenzie and Clough, J. *Chem. Soc.*, 103,687 (1913).

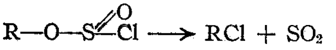
[5] Ruzicka and Liebl, Helv. *Chim. Acta,* 6,278 (1923).

[6] Richter, Ber., 49,2339 (1916).

[7] Badische Anilin und Sodafabrik, *C.* A., 13,324 (1919).



$$ROH + SOCl_2 \longrightarrow R{-}O{-}S(=O){-}Cl + HCl \qquad (I)$$



$$R{-}O{-}S(=O){-}Cl \longrightarrow RCl + SO_2 \qquad (II)$$

McKenzie and Clough[4] obtained an intermediate product, d-amyl chlorosulfinate, from which sulfur dioxide was eliminated according to Equation II. An excess of thionyl chloride was used in this reaction. Cholesterol, in the presence of an excess of thionyl chloride, with or without the addition of a small amount of pyridine, yielded cholesteryl chloride almost quantitatively. When an excess of pyridine was used and the reaction was carried out in ether, a small amount of *bis*-cholesteryl sulfite was also formed. When an excess of thionyl chloride is added to diacetone-glucose in ether and in the presence of an excess of pyridine, little or no sulfur dioxide is eliminated upon refluxing the reaction mixture. When poured into water which is kept slightly alkaline with sodium carbonate, the compound which is formed is hydrolyzed and diacetone-glucose is immediately regenerated. Green[8] has isolated a reactive intermediate product, dichlorothionyl quinol, from which sulfur dioxide was not eliminated by heat under the conditions of the reaction.

Experimental Part

Bis-cholesteryl **Sulfite.**—Two grams of anhydrous cholesterol was dissolved in 50 cc. of dry pyridine. A little in excess of the theoretical amount of thionyl chloride was then added. This mixture was allowed to stand for twenty-four hours at room temperature. At the end of this period water was slowly added until no more precipitate settled out. The impure neutral sulfite ester was filtered off and extracted with a small quantity of hot alcohol to remove any unchanged cholesterol. The ester was purified by several recrystallizations from ethyl acetate; m. p. 186.5–187°. The yield was almost quantitative. Acknowledgment is made for the assistance of two senior students, Karl S. Hecht and Meyer H. Zuravin.

Anal. Calcd. for $C_{54}H_{90}O_3S$: S, 3.91. Pound: S, 4.02.

Bis-cholesteryl sulfite is soluble in cold petroleum ether, carbon tetrachloride, chloroform and ethyl ether. It is only slightly soluble in boiling methyl or ethyl alcohol and acetone. It is only slightly soluble in cold ethyl acetate but very soluble at the boiling temperature. The ester is quite stable to aqueous acid or alkaline saponification. It can be quickly hydrolyzed by boiling in 30% alcoholic potassium hydroxide with a quantitative yield of cholesterol.

This sulfite ester is partially converted into cholesteryl chloride when heated with phosphorus pentachloride in carbon tetrachloride. A small quantity of cholesterol and some unchanged sulfite were also isolated from the reaction mixture. The end-products would indicate that the reaction had gone in the same way that Michaeiis[9] found for the action of phosphorus pentachloride upon diethyl sulfite. The sulfurous acid esters of ethyl alcohol, butyl alcohol and phenol were prepared in a similar manner.

Bis-**(diacetone-glucose)-sulfite.**—Five grams of diacetone-glucose and 100 cc. of pyridine were dissolved in 50 cc. of dry ethyl ether; 0.72 cc. of thionyl chloride was added a drop at a time. The mixture was permitted to stand for three hours. The pyridine

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[8] Green, *J. Chem. Soc.*, 500 (1927).

[9] Michaelis, *Ber.*, 7, 1074 (1874).

hydrochloride which had separated was removed by decantation. The reaction mixture was poured into three volumes of water which was kept faintly alkaline with sodium carbonate. After complete neutralization the ether-soluble portion was separated from the water-soluble constituents. The ether solution was dried over anhydrous sodium carbonate. When the ether was removed under reduced pressure, a yellow transparent syrup remained which had all of the properties of *bis*-(diacetone-glucose)-sulfite. Tests showed the presence of sulfur but no chlorine. The product was identified by hydrolysis with 0.1 *N* alcoholic potassium hydroxide. Potassium sulfite and diacetone-glucose resulted.

Cholesteryl Chloride.—To 5 g. of cholesterol and 1 cc. of pyridine, 10 cc. of thionyl chloride was added rapidly. The reaction mixture was kept cool with running water and was refluxed for one hour. Sulfur dioxide was liberated. The mixture was cooled, poured into water and then extracted with ether. The ethereal solution was dried over anhydrous sodium carbonate. When the solvent was removed under reduced pressure a semi-crystalline product remained. This was recrystallized from alcohol and identified as cholesteryl chloride; m. p. 95–96°. The yield was almost quantitative. The reaction was repeated without the addition of pyridine with identical results.

Ethyl chloride, and butyl chloride were prepared in a similar manner. Attempts to prepare chlorobenzene from phenol by this method were unsuccessful.

Reaction of Diacetone-glucose with Excess Thionyl Chloride.—Five grams of diacetone-glucose and 10 cc. of dry pyridine were dissolved in 30 cc. of dry ethyl ether; 10 cc. of thionyl chloride was added rapidly and the reaction mixture was kept cool by immersion in ice water. It was refluxed for one hour. The pyridine hydrochloride which separated was removed by decantation and the solution poured into ice water. The ether-soluble portion was separated and dried over anhydrous sodium carbonate. When the solvent was removed under reduced pressure a semi-crystalline mass remained which contained sulfur and a trace of chlorine. Upon recrystallization from high-boiling petroleum ether about 3 g. of diacetone-glucose separated; m. p. 102°. Hydrolysis of the remaining sirup with alcoholic potassium hydroxide yielded diacetone-glucose, potassium sulfate and potassium sulfite. It is hoped that a further study of this reaction will result in the production of the chloride.

A similar reaction with cholesterol yielded about 80% of cholesteryl chloride and about 20% of *bis*-cholesteryl sulfite.

Summary

1. The synthesis of *bis*-cholesteryl sulfite is reported and some of its properties are described.

2. The action of thionyl chloride, in the theoretical amount, upon cholesterol and certain other alcohols in the presence of an excess of pyridine yields the sulfurous acid ester of the alcohol. No chlorination takes place.

3. The action of thionyl chloride, in large excess of the theoretical amount, upon cholesterol and certain other alcohols in the presence of an theoretical amount of pyridine, yields the chloride of the alcohol. Evidence is presented to indicate that an intermediate compound is formed which upon heating may break down to form sulfur dioxide and the alkyl chloride.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

STUDIES IN THE CHLOROPHYLL SERIES. I. THE THERMAL DECOMPOSITION OF THE MAGNESIUM-FREE COMPOUNDS

BY J. B. CONANT AND J. F. HYDE

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Chlorophyll a is the magnesium derivative of phaeophytin a, which contains the groupings $—OC_{20}H_{39}$ and $—OCH_3$ presumably as ester groups. By the replacement of the phytol alcohol radical by methyl, methyl phaeophorbide *a* results, which contains, therefore, two methoxyl groups. The replacement of the phytyl group by hydrogen produces phaeophorbide a, a monobasic acid, from which by alkaline hydrolysis the dibasic acid chlorin *e* is formed. In this last reaction a deep-seated change has probably taken place in addition to hydrolysis.[1] A similar set of transformations of chlorophyll *b* yields methyl phaeophorbide *b*, phaeophorbide b and rhodin g.

We have found that all of these magnesium-free compounds lose carbon dioxide when heated in dilute diphenyl solutions to 180–250°. The process may be followed quantitatively by passing nitrogen through the solution and absorbing the carbon dioxide in the usual way. Crystalline products may be isolated by dissolving the reaction mixture in ether and fractionating with hydrochloric acid according to the Willstatter–Mieg procedure.[2] The results are summarized in Table I.

It is evident from an inspection of Table I that all the magnesium-free derivatives of both the a and the *b* series which we have examined, with the exception of the trimethyl ester of chlorin *e*, lose carbon dioxide under the conditions of our experiment. The phaeophorbides lose one molecule of carbon dioxide whereas chlorin *e* and rhodin g lose two molecules. The analyses of the crystalline products which we have isolated in the a series correspond to the loss of the number of moles of carbon dioxide noted in our quantitative decompositions. Definite but irregular amounts of water are formed in the reaction, as shown by the increase in weight of the calcium chloride absorption tube, but the blank was so large that no conclusions could be drawn from the results. It is possible that water may be eliminated and then added during the isolation of the products.

It is significant that the trimethyl ester of chlorin e does not lose carbon dioxide, whereas methyl phaeophorbide *a* loses one molecule. Since the methyl phaeophorbide contains no free carboxyl group, this carbon dioxide must come from some special grouping of the molecule. The decomposition of an ester group is made unlikely by the fact that chlorin e trimethyl ester does not lose carbon dioxide on heating. A lactone seems to be the

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[1] Willstätter and Stoll, "Investigations on Chlorophyll," translated by Schertz and Merz, Science Printing Company, 1928, p. 25.

Willstätter and Mieg, *Ann.*, 350, 1 (1906).

TABLE I

SUMMARY OF DATA OBTAINED IN THE THERMAL DECOMPOSITION OF THE MAGNESIUM-FREE CHLOROPHYLL COMPOUNDS

(1) a Series

Substance	Moles of CO_2 per mole	Temp. in oil-bath, °C.	Time of heating, hours	Product	Yield, %
Methyl phaeophorbide a	0.84	200–240	6.6	Methyl	21
(m. w. = 614)	0.70	220–250	7.0	pyrophaeo-	..
	0.94	250	4.0	phorbide a	21
Phaeophorbide a	1.2	210–225	4	Pyrophaeo-	..
(m. w. = 600)	1.1	220–240	4	phor-	23
	1.1	200–250	1	bide a	
Chlorin *e*	0.94	140–150	1	Pyrochlorin *e*	20
(anhydrous) (m. w. = 630)	1.91	140–170	6	Pyrochlorin *e* Porphyrin	23 3
	2.0	250	5	Pyrochlorin *e* Porphyrin	4 15
	1.9	250	11		..
	1.4	160–175	2.5		..
Chlorin *e* (Lactam hydrate)	1.6	160–185	2.5	Pyrochlorin *e* Porphyrin	44 3
	1.8	240–250	3		..
Chlorin *e* trimethyl ester	0.07[a]	250	3	Unchanged ester	
(2) b Series (products not yet isolated)					
Methyl phaeophorbide b	0.83	220–230	3		
(m. w. = 638)	0.62	250	0.5		
Phaeophorbide *b*	0.98	250	1.5		
(m. w. = 624)	1.3	250	4.0		
Rhodin g (m. w. = 640)	1.9	250	8		

[a] Within the experimental error (±0.8 mg.).

The molecular weights used in calculating the number of moles of carbon dioxide are given; because of the uncertainties of the analyses these values are only approximate.

most probable explanation. As pointed out in our preliminary notice of this work,[3] these results point to the presence of some such grouping as an unsaturated lactone bridge which could lose carbon dioxide.

Methylation experiments now in progress should yield further evidence in regard to the presence of a lactone linkage or a hydroxyl group. The fact that the spectra of the parent substances and the pyro compounds are so similar suggests that the pyrrole rings are in the same condition in both compounds.

Our analytical data, as well as the recently published results of Treibs[4] and of Fischer[5] indicate that there are five or six oxygen atoms in the

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[3] Conant and Hyde, *Science*, 70, 1806 (1929).

[4] Treibs and Wiedemann, *Ann.*, 471, 146 (1929).

[5] Fischer and Baümler, *ibid.*, 474, 65 (1929).

phaeophorbide *a* molecule. The grouping $—COOCH_3$ is clearly present in methyl phaeophorbide and, if one accepts the conclusion that a lactone group is also present, this leaves the extra methoxyl group without sufficient oxygen to constitute a carbomethoxy group if there are but five oxygens. It should be pointed out, however, that there is no clear evidence that there are two carbomethoxy groups in methyl phaeophorbide a. The second methyl group may well be present as the methyl ether of an enol, for example, the enol of a lactam. A similar interpretation is possible with chlorin *e;* indeed, the fact that it is possible to obtain the trimethyl ester by the action of diazomethane on chlorin e as shown by Treibs[4] seems to us strong evidence that the third methyl group in this instance is derived from an enol and not by the opening of a lactone or lactam ring. There seems to be no reason to believe that diazomethane would be effective in opening such groups.

Pyro-phaeophorbide a is an acid; this shows that the carbon dioxide from this compound must have resulted from some group other than the free carboxyl and that the acidic group in phaeophorbide *a* is stable at high temperatures. The final decomposition by alkali of all the compounds we have been mentioning leads to porphyrins,[1,5] which contain the very stable grouping $—CH_2CH_2COOH$; it is quite clear that it is this carboxyl group which is free in phaeophorbide a and which is, therefore, attached to the phytyl group in phaeophytin and in chlorophyll.

The two products formed by the pyrolysis of chlorin e we shall designate by the terms pyrochlorin e and pyrochlorin e-porphyrin. The former substance is green and has a spectrum somewhat similar to that of chlorin e itself, whereas the porphyrin has the general appearance, spectrum and characteristics of this very large class of substances. The two compounds are isomeric. The green pyrochlorin e is unstable and on standing for a few months undergoes a partial decomposition. By acid fractionation it is possible to obtain from the decomposed material a substance which is very similar to pyrochlorin e-porphyrin, but not identical with it. It is clear that in the pyrolysis of chlorin e we have stripped the molecule of all but one carboxyl group and in the green substance have a relatively simple representative of the chlorophyll series, which still has a spectrum similar to the more complex members. A further study of these products, as well as those from the b series and the magnesium-containing compounds, is now in progress and should throw more light on the question of the structure of the first transformation products of chlorophyll. It seems extremely probable that the carbon skeleton of the chlorophyll porphyrins as established recently by Fischer[6] is present in all the chlorophyll series, as he has indicated. The ease of transformation of our green

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[6] Fischer and Treibs, Ann., 466, 188 (1928); Fischer and Schormüller, *ibid.*, 473, 211 (1929).

pyrochlorin e into a porphyrin is more evidence pointing in this same direction.

In connection with the analytical data given in the experimental part of this paper, it should be mentioned that it is impossible to decide at present between several possible formulas for each compound. The same difficulties have been encountered by other workers in this field as pointed out by Fischer.[4] We have given the calculated values for several different formulas in each case. Of the more probable formulas for methyl phaeophorbide *a* ($C_{36}H_{38}O_6N_4$, $C_{36}H_{38}O_5N_4$, $C_{35}H_{38}O_6N_4$, $C_{35}H_{38}O_5N_4$) we prefer the formula $C_{36}H_{38}O_6N_4$, since all our results can be best interpreted on this basis. Our analyses and quantitative results of pyrolysis are consistent in each case. At first sight, there appears to be a certain inconsistency between the formulas of the monobasic porphyrins and our pyro-compounds from chlorin e. The recent work of Fischer[6] has established that there are 31 carbon atoms and 2 oxygen atoms in the chlorophyll monobasic porphyrins, yet our substances, which should be isomeric, have at least 32 carbon atoms and 3 oxygen atoms. It would seem that our method of decomposition has left some group in the molecule which is eliminated through the usual alkaline decomposition; it will be a matter of great interest to determine the nature and position of this grouw.

Experimental Part

Preparation and Analysis of Methyl Phaeophorbide a, Phaeophorbide *a,* Chlorin e and Chlorin e Trimethyl Ester.—Phaeophytin was used for the preparation of these substances. In all cases the methods of preparation used were those described by Willstatter and Stoll.[1] The products were all obtained in a nicely crystalline condition, and agreed closely in acid number, spectrum and crystal form with the descriptions given by the same authors. In most eases, however, the yields obtained were only one-half to two-thirds of those mentioned by Willstatter and Stoll.

In the preparation of chlorin e by using the cold hydrolysis over a long period of time, the product seemed to correspond to the form described as the lactam hydrate, while in other cases, using hot hydrolysis with pyridine, the so-called anhydrous form was obtained. Chlorin e trimethyl ester was prepared both by using dimethyl sulfate according to Willstatter, and according to Treibs and Wiedemann using diazomethane.[4] Both products melted on the block at 202–204° and a mixed melting point showed no depression.

For analysis the materials were in most cases redissolved in ether and refractionated with hydrochloric acid to insure purity. In all cases the samples were dried over phosphorus pentoxide for a period of from three to five days at a pressure of 10–20 mm. The following table gives the analytical results; these and all the other results reported in this paper were obtained by the Pregl micro methods.

And. Methyl phaephorbide a: C, 70.38, 70.90, 71.21, 69.70; H, 6.23, 5.95, 6.06, 6.16; N, 9.38, 9.53, 9.33. Phaeophorbide a: C, 67.96, 68.72, 68.29, 68.00; H, 5.94, 6.10, 6.20, 6.53; N, 9.33. Chlorine: C, 67.14; H, 6.49; N, 8.81, 8.96. Chlorin e trimethyl ester: C, 69.78, 69.03; H, 7.25, 6.88; N, 8.75.

Preparation of Pyro-compounds.—The method of pyrolysis involved heating the substance in diphenyl solution to the desired temperature for the required length of time.

The apparatus consisted of a side arm U-tube made from tubing thirty millimeters in diameter, and was about 150 mm. in height. This tube contained the diphenyl solution and was heated in an oil-bath. The outlet tube was attached to a 200-mm. length of 3-mm. tubing bent in the form of a U-tube. This served as an air-condenser to assist in preventing diphenyl from being carried along in the gas stream. To this tube was attached another U-tube containing calcium chloride followed by a potash absorption bulb. The whole system was swept out during the experiment by a slow stream of dry nitrogen, which served to agitate the diphenyl solution as well as to transfer any carbon dioxide or water formed to the absorption train. By frequent weighing of the absorption tubes the progress of the decomposition could be followed. The outlet side of the reaction tube was surrounded by a small copper cooling coil to prevent the diphenyl from distilling

In starting an experiment, 20 g. of diphenyl was heated to boiling for a short time, a slow stream of nitrogen being passed through the apparatus. The absorption tubes were then weighed, replaced and the heating continued for one to three hours to determine any blank which might be involved. The blank on the carbon'dioxide tube was negligible while that on the water tube was usually about a milligram per hour. The sample (150–50 mg.) was then introduced quickly into the hot diphenyl and the heating carried out at the desired temperature.

The results of the pyrolysis experiments have been summarized in Table I; some typical results are given in more detail below. Pyrolysis of chlorine e: temp., 160–175°; time, 2.5 hrs.; 0.1137 g. yielded 0.0116 of CO_2 and 0.003 g. of H_2O after subtracting a blank of 0.002 g. (0.0008 g. per hr.). Temp. 250°; time 5 hrs.; 0.1252 g. yielded 0.0171 g. of CO_2 and 0.0024 g. of H_2O after subtracting a blank of 0.0060 g. Because of the large blank (due to the volatility of the diphenyl), not much significance can be attached to the increase in weight of the calcium chloride tube. However, some water appears to be formed and in one experiment with chlorin *e* it was condensed in a freezing mixture.

The products were all purified in the same way. The reaction mixture was dissolved in 300 to 500 cc. of ether and fractionally extracted with various concentrations of hydrochloric acid according to the method of Willstatter and Mieg. The main acid fractions were then washed twice with ether to remove any traces of diphenyl and the colored substance retransferred to ether either by dilution of the acid layer or by partial neutralization with ammonia. These ether solutions were then washed with water or with very dilute potassium hydroxide in the case of an alkali insoluble product, dried with sodium sulfate and concentrated to a small volume. Usually concentration to 10 or 15 cc. caused the material to crystallize. For purification these materials were dissolved in ether and refractionated with acid.

The yields given in the table are obviously not true measures of the amounts of the compounds formed in the reactions; the losses during purification of such small samples are very large. In no case was the formation of carbon monoxide detected. In most cases a few milligrams of black ether-insoluble residue was found in the reaction mixture. In one instance, using a 0.5-g. sample of chlorin e and adding to the cold diphenyl, 0.3 g. of this black residue was formed. It would thus seem desirable to add the sample to the hot diphenyl.

Chlorin e trimethyl ester was the only substance recovered from the reaction mixture unchanged.

Methyl Pyrophaeophorbide a.—This substance crystallizes from ether in beautiful long flat needles which tend to grow in radiating clusters. Their color is deep blue with a metallic luster. The crystals redissolve readily though slowly in ether imparting to it an olive-green to brown color, indistinguishable from that of an ether solution of pure methyl phaeophorbide a. It dissolves very readily in pyridine and rather slowly in acetone. The acid number is 15, the acid extract being colored a greenish-blue. The product is not itself extracted from ether by mild alkali but is hydrolyzed slowly in acid solution yielding a material which can be extracted with alkali. This substance is identical in acid number, spectrum and behavior toward alkali with pyrophaeophorbide *a*. The melting point of methyl pyrophaeophorbide *a* on the block is 220–225°. The spectrum by visual comparison is identical both in position and relative intensities with that of pure methyl phaeophorbide *a*. Unlike methyl phaeophorbide *a*, the pyro-compound does not give the phase test.

The spectra given below and with the other new compounds were measured in ether solution (concn. 0.1 g. per 5 liters), the thickness of the solution is given in mm. Dotted lines indicate fainter absorption.

100 mm.: 701.2---689.9—646.8; 622.9---619—601.2--597.4; (hazy) 565.6—553.5; 542.7—529.5; 519.2—491.7; 478.6—464.6; E. A. 444.6.

20 mm.: 679.5—656.3; 617.8—603.4; 540.1—531.9; 512.1—504.2---494.7; E. A. 433.

Anal. Calcd. for $C_{35}H_{38}O_4N_4$: C, 72.66; H, 6.57; N, 9.68—for $C_{35}H_{38}O_3N_4$: C, 75.00; H, 6.79; N, 9.65—for $C_{34}H_{38}O_4N_4$: C, 72.1; H, 6.72; N, 9.9—for $C_{34}H_{38}O_3N_4$: C, 74.2; H, 6.9; N, 10.2. Found: C, 74.03, 73.83, 73.93; H, 6.40, 6.04, 6.03; N, 10.14, 10.14, 9.90.

Pyrophaeophorbide a.—This substance was extracted from ether solution by 13–14% acid to give a bluish-green solution. Its acid number is between 12 and 13. It crystallizes from ether in a micro-crystalline condition, probably needles, with a steel blue luster. The ether solution is colored olive-green to brown, practically identical in color with a solution of pure phaeophorbide *a*, and possesses the same reddish fluorescence. Toward other solvents its behavior is the same as phaeophorbide *a*. With dilute alkali an ether solution gives a yellowish-brown precipitate at first which gradually redissolves in the ether as well as the water layer, imparting a brown color suggestive of the phase test. It appears to give the phase test. On the block it melts between 210 and 220°. Spectroscopically this product is identical with phaeophorbide *a*, which is in turn identical with methylpyrophaeophorbide *a*.

20 mm.: 682.0---679.7—657.6---655.0; 615.4--604.4; 549.0—531.6; 512.9—491.5; E. A. 433.7.

100 mm.: 699.1---687.3—647.5---644.0; 621.6---619—601.7; 565.5—555.9; 541.0—529.4; 517.2—491.0; 481.3—462.1; E. A. 443.6.

Anal. Calcd. for $C_{34}H_{36}O_4N_4$: C, 72.34; H, 6.38; N, 9.92—for $C_{33}H_{36}O_4N_4$: C, 71.7; H, 6.52; N, 10.13—for $C_{34}H_{36}O_3N_4$: C, 74.4; H, 6.57; N, 10.21—for $C_{33}H_{36}O_3N_4$: C, 73.88; H, 6.71; N, 10.44.

In the formation of pyrophaeophorbide *a* there was obtained as a by-product a small amount of black micro-crystalline material. It was extracted from the mother liquor by 9% acid giving a green solution, and on retransferring to ether gave a dark purple-red color which was unusually intense considering the amount of material present. The quantity was too small for careful investigation, but the spectrum is given below.

20 mm.: 670.0—661.6; 588.4--579.5; 566—557.2—546.2; 525—497.4; E. A. 441.7.

100 mm.: 675—653.0; 604---591.9—580.3---574.8; 568.1—557.1---543; 527.3—494.3; E. A. 452.7.

Pyrochlorin *e*.—Pyrochlorin e is extracted from an ether solution by 8% acid, giving a deep greenish-blue solution. Its acid number is between seven and eight. It is so soluble in ether that the small quantities available could not be crystallized from that solvent. It was, however, obtained in a micro-crystalline condition by removing most of the ether, adding a small volume of ethyl alcohol and diluting gradually (over a period of a day) with water to 50%. Prepared in this way it appears as a dark blue micro-crystalline powder. The color of its ether solution is identical with that of chlorin *e*. However, when the solution is shaken with dilute potassium hydroxide, the behavior is similar to that of an ether solution of pyrophaeophorbide *a*. A brown precipitate appears which only partially redissolves and colors both the ether and water layers yellowish-brown, a color suggesting the phase test. Its melting point is between 165–170°.

The spectrum is the same as that of chlorin e in relative intensities, but the corresponding lines are shifted slightly to shorter wave lengths, most noticeably in the red.

20 mm.: 670—649.3; 609—596.0; 532.3—525.5; 509.6—487.3; E. A. 430.8.

100 mm.: 679.6—641.1; 611.9—596.6; 560.9—550.2; 534.1—526.1; 516.5—483.4; E. A. 442.9.

Anal. Calcd. for $C_{33}H_{38}O_3N_4$: C, 73.60; H, 7.06; N, 10.40—for $C_{32}H_{36}O_3N_4$: C, 73.28; H, 6.87; N, 10.68. Found: C, 73.70, 74.14, 73.79, 73.52; H, 6.86, 6.96, 5.87, 6.04; N, 10.41, 10.26, 10.35.

Pyrochlorin e seems to be unstable; a carefully purified sample of the solid, after standing for three months, on refractionation with acid yielded a small quantity of material which was extracted with 1% acid. This material was red in ether solution and crystallized in beautiful ruby-red prismatic needles. The color of the ether solution and acid number suggest identity with pyrochlorin *e* porphyrin (isomeric with pyrochlorin *e*). The spectrum, however, seems slightly different.

50 mm.: 666.1—659.3---655.5—647; 594.1---582—574.8; 551.1—533.9; 522.3—487.2; E. A. 452.8.

Pyrochlorin e **Porphyrin.**—This substance was formed as a by-product in rather small quantities along with pyrochlorin *e*. It is extracted from the mother liquor easily with 1% acid and the acid number is between one-half and one. The acid solution is purple and gives a red ether solution on retransferring. The concentrated ether solution gives long red prismatic needles with a purplish-blue iridescence. The solubility was similar to that of phylloporphyrin. By shaking the ether solution with dilute potassium hydroxide, a rather insoluble potassium salt is formed.

20 mm.: 589.1---580.2—573.4; 548.1—533.4; 516—491.0; E. A. 433.3.

100 mm.: 665.6-657.5---651.0; 634.7—628.8; 593.4---580.9—573.5; 547.3—532.2; 519.3—487.0; E. A. 446.3.

Anal. Calcd. for $C_{33}H_{38}O_3N_4$: C, 73.60; H, 7.06; N, 10.40—for $C_{32}H_{36}O_3N_4$: C, 73.28; H, 6.87; N, 10.68. Found: C, 74.03, 74.23, 74.02; H, 6.31, 6.81, 6.73; N, 10.37, 10.67, 10.73.

Summary

1. Phaeophorbide *a*, methyl phaeophorbide *a* and chlorin *e* lose carbon dioxide on heating in dilute diphenyl solution to 180–250°. The amount of carbon dioxide evolved corresponds to the loss of one molecule with the phaeophorbides and two in the case of chlorin *e*. The analyses of the crystalline products confirm this conclusion. Two isomeric products are obtained from chlorin *e*, one a green substance the other a porphyrin.

2. The experiments with the phaeophorbides indicate that a lactone or similar grouping is the source of the carbon dioxide and that the phytol in phaeophytin is attached to the $—CH_2CH_2COOH$ group.

CAMBRIDGE, MASSACHUSETTS

NOTE

The Decomposition of Methyl-2-hexanol-2.—Recently, Edgar, Calingaert and Marker[1] have described the preparation of methyl-2-hexanol-2. The olefin formed by slow distillation of this tertiary alcohol with a trace of iodine was stated to be methyl-2-hexene-2, but the isomeric methyl-2-hexene-1 may also have been present. Hydrogenation of either of these heptenes would produce 2-methylhexane, and since this was the desired product no study was directed to identify the olefins which may have been produced.

In 1927 we studied this problem and obtained evidence to show that a single olefin, presumably methyl-2-hexene-2 (later called "Heptene-A), was formed when the alcohol was refluxed without catalyst for several hours. This decomposition always occurs to a small extent during distillation at atmospheric pressure (139–141"). Apparently, methyl-2-hexanol-2 does not undergo scission into "acetone + butane" or into "methyl butyl ketone + methane," since no ketones could be isolated from the distillate. This type of scission is known to occur in similar cases at more elevated temperatures.[2] At 58–60' and 20 mm., methyl-2-hexanol-2 may be distilled repeatedly without decomposition. When purified in this way the index of refraction was n_D^{20} 1.4187.

With a small amount of iodine as catalyst, as in the work of Edgar, Calingaert and Marker, the extent of the dehydration was found to be much greater and the nature of the "Heptene-B" thus produced differed from Heptene-A. This difference displayed itself in the refractive index and in the properties of the respective heptene dibromides. Both heptenes boiled at 92–95°.

The index of refraction values for Heptene-B were: 18.5°, 1.4098; 19.0°, 1.4091; 20.5°, 1.4088; 23.5°, 1.4054. The corresponding values for Heptene-A at 17.5 and 20.5° were 1.4049 and 1.4040, respectively. This difference is certainly large enough to be significant. The density of Heptene-B at 20° was found to be 0.7089.

The dibromides were prepared by adding the calculated quantity of pure bromine drop by drop to each of the heptenes. The reaction flasks were cooled in ice water during this addition. The dibromide of Heptene-A distilled at 99–100° (27 mm.) and the pure compound gave the following values for n_D: 18°, 1.5020; 19°, 1.5014; 19.8°, 1.5010; 22°, 1.5001.

Anal. Calcd. for $C_7H_{14}Br_2$: Br, 62.0. Found, 62.6.

This dibromide boiled with decomposition at 187–188° at ordinary pressure.

The dibromide of Heptene-B, similarly prepared, and fractionally distilled in *vacuo*, yielded a fraction boiling at 65–70' (18–19 mm.) with

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[1] Edgar, Calingaert and Marker, THIS JOURNAL, 51, 1485 (1929).

[2] See Grignard and co-workers, *Compt. rend.*, 176, 1860 (1923); 182, 299 (1926); *Ann. chim.*, 2, 298 (1924).

$n_D^{17.5}$ 1.4700, and 1.6 times as much of a higher fraction, b. p. 93–97° (17–18 mm.), with $n_D^{17.5}$ 1.5022. Of these two fractions, the latter seemed identical with the dibromide from Heptene-A.

To explain these data, it is suggested that "Heptene-A" is largely or entirely methyl-2-hexene-2, and that "Heptene-B" is a mixture of methyl-2-hexene-2 and methyl-2-hexene-1, the former predominating.

Summary.—Methyl-2-hexanol-2 slowly undergoes dehydration into methyl-2-hexene-2 by refluxing. With iodine as a catalyst, the dehydration reaction proceeds more readily but methyl-2-hexene-1 also appears to be formed.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
NORTHWESTERN UNIVERSITY
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ADDITIONS AND CORRECTIONS

1921. VOLUME 43

Indirect Method of Preparation of Organic Mercuric Derivatives and a Method of Linking Carbon to Carbon, by Morris S. Kharasch.

Page 2243. The author writes as follows: ". . . Lines 22 and 34 should read '2,2′,4,4′,6,6′-hexanitro mercury diphenyl' instead of '2,2′,4,4′,6,6′-hexanitro diphenyl.' It is unfortunate that this omission of the word 'mercury' has occurred. The author intended to call attention to the very interesting fact that if the molecule of 2,4,6-trinitrophenyl mercuric chloride is treated with potassium periodide at room temperature, two simultaneous reactions take place. The first reaction is a substitution of the —HgX radical by iodine and the second reaction is a 'bridging' effect due to the potassium iodide.

"This is believed to clear up the apparent discrepancy in the article and results recorded in a recent publication [Whitmore and Thurston, THIS JOURNAL, 51, 1502 (1929)], except that since these authors refluxed the sample of 2,4,6-trinitrophenyl mercuric chloride with iodine for eight hours and did not employ potassium iodide at all, they could not have noted the formation of the 2,2′,4,4′,6,6′-hexanitro mercury diphenyl, as observed by the first author. It is the unusual speed of formation of this latter compound from 2,4,6-trinitrophenyl mercuric chloride and potassium iodide at ordinary temperature that was deemed worthy of mention."—M. S. KHARASCH.

1928. VOLUME 50

The Analysis of Mixtures of Ethyl Alcohol, Ethyl Acetate, Acetic Acid and Water, by S. Poznanski.

Page 986. Line 3 from the end should read: ". . . This method has the advantages that the unknown acid and standard dissociate equally in solution, . . ."

Page 988, line 4 from the end, insert "of a per cent." after "thousandths."—S. POZNANSKI.

The Iodide, Iodine, Tri-iodide Equilibrium and the Free Energy of Formation of Silver Iodide, by Grinnell Jones and B. B. Kaplan.

Page 1856. In Table IIA the second entry in the last column should read "0.0011364" instead of "0.001364."—GRINNELL JONES.

The Normal Potential of the Iodine–Iodide Electrode, by Grinnell Jones and B. B. Kaplan.

Page 2073. In Table IVA the *E* value at the foot of the last column should read "–0.25435" instead of "–0.254356."—Grinnell Jones.

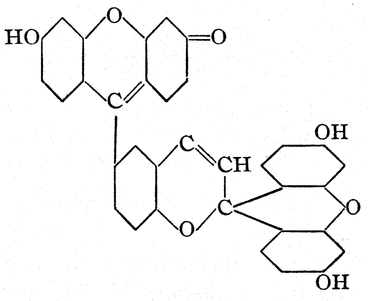
The Atomic Weight of Cesium, by Theodore W. Richards and Marcel Françon.

Page 2162. A note of correction has been received as follows: ". . . Professor Honigschmid has pointed out a mistake in the calculation of one of the results. The second of the analyses reported should give for the atomic weight of cesium 132.841 instead of 132.832; the average is thus 132.811 instead of 132.809. This slight difference is unimportant and the result confirms, as before, the adopted value of 132.81."—Marcel Françon.

6-Aldehydo-coumarin and Dyes Derived from It, by Rajendranath Sen and Dukhaharan Chakravarty.

Page 2430. Footnote 5 should read "Sen and Guha Sarkar, *J. Indian Chem. Soc.,* 1,150–172 (1924)."

Page 2431. Formula III should read



Rajendranath Sen

1929. Volume 51

Trimethylacetaldehyde and Dimethylethylacetaldehyde, by J. B. Conant, C. N. Webb and W. C. Mendum.

Page 1247. Line 5, for "$H_2C(OCR_3)_2$" read "$H_2C(OCH_2CR_3)_2$." Line 6, for "tertiary alcohols" read "carbinols."

Page 1249. Line 12 of Experimental, for "Di-*tert.*-butyl Acetal of Formaldehyde, $H_2C(OC(CH_3)_3)_2$" read "Di-*tert.*-butyl-carbinol Acetal of Formaldehyde, $H_2C(OCH_2C(CH_3)_3)_2$."

Page 1250. Line 6, for "$C_9H_{20}O_2$" read "$C_{11}H_{24}O_2$." Line 12 from end, for "Di-*tert.*-amyl Acetal of Formaldehyde, $H_2C(OC_5H_{11}$-*tert.*$)_2$" read "Di-*tert.*-amyl-carbinol Acetal of Formaldehyde, $H_2C(OCH_2C_5H_{11}$-*tert.*$)_2$." Line 3 from end, for "$C_{11}H_{24}O_2$" read "$C_{13}H_{28}O_2$."—J. B. Conant.

Phenol-halo-phthaleins. Preliminary Paper, by F. F. Blicke and F. D. Smith.

Page 1867. Footnote 8 should read "Blicke and Smith, This Journal, 51, 1948 (1929)."—F. F. Blicke.

Halogen-Substituted Aromatic Pinacols and the Formation of Ketyl Radicals, $R_2(IMgO)C$—, by M. Gomberg and John C. Bailar, Jr.

Page 2236. Line 9 from the end, for "substituted" read "unsubstituted."—John C. Bailar, Jr.

Isomers of 2-pentene. III. The Ultraviolet Absorption Spectra of the Isomeric 2-Pentenes, by Emma P. Carr.

Page 3052. The last part of Footnote 10 should read "Scheibe. May and Fischer, Ber., 57,1332 (1924)."

Chemical Kinetics in Highly Dilute Solution. Bromo-acetate and Thiosulfate Ions in the Presence of Sodium Ion at 25°, by Victor K. La Mer.

Page 3341 The author writes as follows: "... An unfortunate error was made in computing the ionic strengths of the final solutions. The contribution of the sodium thiosulfate to the ionic strength was computed in terms of a normal solution of valence type $(1, -2)$, whereas the normality employed was really in terms of iodine equivalents, *i. e.*, for thiosulfate $\mu = 3$ N and not 1.5 N. The net result is that each value of μ given in the article must be multiplied by a factor $40/25 = 1.60$ and each $\sqrt{\mu}$ by $\sqrt{1.60}$ or 1.265. This correction distorts Fig. 1 slightly and thereby weakens but does not destroy the conclusions reached. Thus the limiting experimental slope $d \ln k/d \sqrt{\mu}$ for the lowest points is not equal to $0.93 Z_A Z_B$ but to about $0.75 Z_A Z_B$. In other words, the limiting theoretical slope $Z_A Z_B$ is being rapidly approached but has not been attained even for the region of dilution of $\mu = 0.002$ to 0.001, for a reaction of such comparatively simple valence type as the one employed. The values given in Table I refer to $\sqrt{\mu}$ and not to μ."—VICTOR K. LA MER.

NEW BOOKS

Lectures on Combustion. By JOSEPH PRIESTLEY, LL.D., F.R.S., and JOHN MACLEAN, M.D., Professor of Mathematics, Natural Philosophy and Chemistry in the College of New Jersey. Edited by WILLIAM FOSTER, Princeton University. Foreword by Professor Hugh S. Taylor. Princeton University Press, Princeton, N. J., 1929. vii + 116 pp. Illustrated. 13 × 21 cm.

This small volume contains, first, a brief, but interesting biography of John Maclean, M.D., the first professor of Chemistry at the College of New Jersey (Princeton) by Professor Foster; second, a reprint of Priestley's famous valedictory pamphlet published in "Northumberland in America" in defense of the doctrine of Phlogiston, and third, "Two Lectures on Combustion and an Examination of Dr. Priestley's Considerations on the Doctrine of Phlogiston" by Maclean in answer to this pamphlet.

Professor Foster's biography shows Maclean as an attractive figure;—practicing medicine successfully and a member of the Faculty of Physicians and Surgeons of Glasgow University at 21; Professor of Chemistry and Natural History at Princeton at 25; an enthusiast for the newest developments of the chemical science of his period.

Priestley's pamphlet displays the skill and clarity of presentation of the accomplished writer and also an appealing modesty; but Maclean in his two lectures points out with vigor and persistency the errors, chiefly of *fact*, on which Priestley's arguments were based.

A Foreword by Professor Taylor states that this volume was issued on the occasion of the dedication of the new chemical laboratory at Princeton. This is indeed most appropriate; the enthusiasm of Maclean for chemistry and his emphasis of the importance of experimental investigations in that science afford a splendid heritage and an inspiring tradition.

ARTHUR B. LAMB

Müller-Pouillets Lehrbuch der Physik. (**Müller-Pouillet's** Textbook of Physics.) **Lehre** von der strahlenden Energie **(Optik).** (The Science of Radiant Energy. Optics.) Eleventh edition. Volume II, second half. Edited by KARL WILHELM MEISSNER. Collaborators: Part I, E. BUCHWALD, M. CZERNY, E. GEHRCKE, G. HETTNER, H. KOHN, R. MINKOWSKI, W. PAULI; Part II, E. BACK, D. COSTER, B. GUDDEN, G. HERTZ, A. KRATZER, R. LADENBURG, L. MEITNER, F. PASCHEN, W. PAULI, R. W. POHL. Friedrich Vieweg und Sohn, Akt.-Ges., Braunschweig, Germany, 1929. Part I, xvi + 799 pp. 498 figs. Part II, xv + 684 pp. 223 figs. 15.5 X **24.5** cm. Price, unbound, R. M. 87.50; bound, R. M. 95.

Three years later than the half-volume on geometrical optics, appears this collective work upon physical optics and related subjects. The decease of Otto Lummer, the original editor, together with the amazing development of the field, provided formidable difficulties for the new editor and for the contributors, as the preface duly explains. In particular a helpful introduction to the new quantum mechanics and to wave mechanics, by Pauli, was included, but time was lacking for revision of other sections which could have been profitably handled from this standpoint. In many cases, however, pertinent references have been provided.

The first part of the half-volume deals with reflection, refraction, dispersion, polarization, the laws of radiation, photometry, spectroscopic and radiometric methods. The section on photometry, together with that on the aims and limitations of technical light production, is highly suggestive and replete with practical applications. Nearly all the other sections reflect the detachment of the pure scientist. The average chemist will seldom feel the need of additional theory, but he could justly protest upon finding rotation of the plane of polarization dismissed with the views of Fresnel and of Airy, plus a very brief list of references to later work.

The second part takes up the structure of various types of spectra, and modern interpretations of the same. Those who have struggled to extract from current physical literature, with its perversely variable notation, a fragmentary knowledge of such interpretations will find here intelligibility, compactness, adequacy, Gratitude should even overbalance exasperation when at the end of the volume, luminescence, photochemistry and photography are found all occupying the Procrustean bed of sixty pages.

Undeniably these two books, at moderate cost, can make good a deficiency which inexcusably exists in many a chemical library.

G. S. FORBES

Gmelins Handbuch der anorganischen Chemie. (**Gmelin's** Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition. Iron. System number 59. Part **A,** Installment **1.** Issued by the Deutsche Chemische Gesellschaft. Verlag Chemie G. m. b. H., Corneliusstrasse **3,** Berlin W 10, Germany, 1929. 226 pp. 17 × 25 cm. Price, to subscribers, M. 26; singly, M. **33.**

Iron has been of such outstanding importance in human affairs since the earliest times that it is not surprising that in this comprehensive handbook two large volumes are to be devoted to this element. One volume (Part A) will contain the sections dealing with the history and occurrence of iron, the metal itself and its alloys; the other (Part B) will cover the compounds of iron. The whole will run to about 1600 pages, and will be published in separate installments of about 200 pages each. The publishers assure us that these will appear in rapid succession.

The first installment, now in hand, contains the sections on the history of iron, on its occurrence and on the preparation of pure iron. As an indication of the magnitude of the field to be covered it may be remarked that the section on the history of iron, occupying 60 pages, is exclusively and merely a tabulation of the literature of the subject. The section on the occurrence of iron (120 pages) discusses the subject both from a geological and a geographical point of view.

These volumes on iron will indeed be welcome. This element was never reached in the seventh edition of the Gmelin handbook and has not yet been reached by the treatises of Mellor or of Abegg.

An imposing array of collaborators has been secured. Those concerned in the preparation of this first installment were H. Ehrenberg, O. Meyer, E. Pietsch, P. Ramdohr and R. Wasmuth.

ARTHUR B. LAMB

Proceedings of the Seventh International Congress of Photography. Edited by W. Clark, T. Slater Price and B. V. Storr. W. Heffer and Sons, Ltd., Cambridge, England, 1929. xiii + 571 pp. Various papers illustrated. 15.5 × 24.5 cm. 25/-net.

On July 9–14, 1928, the Seventh International Congress of Photography met in London. The proceedings of this meeting together with the papers and discussions there presented are now published in full. The meeting was divided into three sections, Section 1 being further subdivided into four subsections: (la) Theoretical Aspects of Photography, in which sixteen papers were presented, ten papers were taken as read, and a report was made on the "Unit of Photographic Intensity." (lb and lc) Photographic Practice and Scientific Applications, in which seven papers were presented and eleven taken as read. (1d) Photo-engraving—ten papers were presented. Only one paper was presented, as a general lecture, in Section 2, "Pictorial Photography: The Relation of Technical Advance to Further Artistic Achievement." In Section 3, Bibliography, Record Photography, History, Patents, Copyrights *and* other Legal *Questions,* eight papers were taken as read and discussed.

To review each individual paper and the discussions which follow them is not possible in the space allotted here. Suffice it to say that the subjects dealt with cover almost every phase of photographic science and practice. "Probably few people reflect," said Mr. Renwick in his opening address, "on the vast changes which have taken place in the methods and in the applications of photography" since the first International Congress in 1899. Who can read these Proceedings, however, without realizing that tremendous strides have been made, and the very great importance of photography in our every-day life and its many connections and ramifications in the various fields of science?

Appendices are included giving the officers of the Congress, the organizing and other committees, regulations, and a list of members and associate members. The whole forms a compact and well arranged presentation of the Congress proceedings.

E. P. WIGHTMAN

Lumineszenz-Analyse im filtrierten ultravioletten Licht. (Analysis by Means of Luminescence in Filtered Ultraviolet Light.) By Professor Dr. P. W. DANCKWORTT, Hannover. Second, enlarged edition. Akademische Verlagsgesellschaft m. b. H., Leipzig, Germany, 1929. viii + 147 pp. 56 figs. 16 X 23.5 cm. Price, unbound, R. M. 8.40; bound, R. M. 9.50.

In his preface to the second edition the author emphasizes his continued self-restraint, evidenced by omission of all theoretical discussions. As a result, the thirty-two additional pages deal exclusively with new apparatus, methods and data. This estimate does not include new material replacing that which has become obsolete since July, 1928. No part of the book remains unchanged, but apparatus, organic compounds, oils and alkaloids receive the most attention. A detailed discussion of porphyrins is added to the biological section. The recording, by photographic methods, of ultraviolet fluorescence has now become important. Its possibilities are illustrated by exposures comparing various textiles and adhesives by reflected daylight, by visible fluorescence light and by ultraviolet fluorescence light. One hundred and twenty new references fortify the bibliography. In every respect the revision has been painstaking and successful.

G. S. FORBES

Die Korrosion, unter Berücksichtigung des Materialschutzes. Vol. I. General and Theoretical Part. (Corrosion, with a Consideration of the Protection of Materials.) By Professor Dr. O. KRÖHNKE, O., Professor Dr. E. MAASS and D. W. BECK. S. Hiizel, Königstrasse 2, Leipzig, Germany, 1929. viii + 208 pp. 43 figs. 15 × 22.5 cm. Price, unbound, M. 16; bound, M. 17.50.

This monograph is to consist of two volumes; the one now at hand, which discusses in general the theory of the corrosion of metals and the protective coatings of metals; and Volume II, which is to discuss in detail the corrosion of the most important technical metals and alloys.

The preparation of this monograph was prompted, according to the Preface, by the lack of such a treatise in the German language and by the inadequate treatment in the English and American treatises of the German literature on corrosion.

The first hundred pages deal with the mechanism of the dissolution of metals, with passivity and with the external causes of corrosion. The presentation is relatively clear, straightforward and non-mathematical. It is particularly valuable for its full discussion of the German investigations in this field.

The next thirty pages contain an account of metallic and non-metallic protective coatings. It is difficult to see how so cursory and superficial a treatment of this subject can be of value to anyone.

The final sixty pages are occupied with indexes and a bibliography.

The book is open to criticism in that while it mentions meticulously the investigators responsible for the various researches, it does not give direct references to their publications. There is, to be sure, the bibliography, but this has no general index, so it is all but impossible to look up the specific research referred to in the text.

ARTHUR B. LAMB

Statistical Mechanics. The Theory of the Properties of Matter in Equilibrium. By R. H. FOWLER, M.A., Fellow and Lecturer of Trinity College and Stokes Lecturer in Mathematics in the University of Cambridge. The University Press, Cambridge, England, 1929. Sole American Agents, The Macmillan Company, 60 Fifth Avenue, New York City. viii + 570 pp. 28 figs. 18.5 X 27 cm. Price, $10.50.

The volume contains a very clear and complete exposition of the equilibrium theory of Statistical Mechanics growing out of the author's study of the physical state of matter along the lines suggested by the announcement for the Adams Prize Essay for 1923.

Chemistry has hitherto been quite content to use thermodynamics as practically the sole basis for correlating its facts pertaining to the chemical equilibrium of substances. During the past two decades, however, there has been an increasing need of supplementing the purely thermodynamical treatment by the methods of the Kinetic or Statistical theory. It cannot, of course, be denied that in pre-quantum times there did not exist a sufficiently general theory adequate for the treatment of the somewhat complicated problems of chemical science. The development of the quantum theory has, however, already supplied, at least in principle, the elements needed to surmount many of the difficulties of the classical statistical theory. Professor Fowler in attempting a practically complete exposition of the theory under the trying conditions presented by the rapidly developing quantum theory, deserves special thanks from those devoted to chemistry. It is to be noted that the new quantum mechanics were established after the manuscript was completed but the changes introduced thereby are, on the whole, insignificant. The final chapter, though terse, indicates sufficiently (perhaps only for the present) the nature of the modifications imposed by the most recent position of the quantum theory.

There have been two earlier expositions of statistical theory published, those by Herzfeld and Smekal following Ehrenfest and Trkal's 1920 paper. Professor Darwin and the author some years ago (1922) developed a new and elegant method of treating statistical problems which has been employed in the present systematic treatment. The method avoids the usual indiscriminate use of Stirling's formula for factorials and, moreover, permits an examination of the average state of an assembly. To be sure the "average state" and "the most probable state" are the same, but the average energy of the assembly may be evaluated by the new method and the partition related to temperature without using Boltzmann's theory relating entropy to probability. The latter process has always been somewhat unsatisfactory, and unconvincing.

The average state is calculated by the use of the multinomial expansion theorem together with a theorem from complex variable theory. In the more general applications multiple complex integrals appear but no special difficulty is created on this account. The new mathematical method has the advantage of precision, power and rigor, and in dealing with the relation of statistical mechanics to thermodynamical principles sheds new light on the nature of entropy. Especially illuminating is the author's criticism of that much mistreated concept "thermodynamical probability" which in the hands of many has sometimes been woefully twisted out of the shape into which it was originally cast by Boltzmann.

The first and second chapters set out and discuss the ideas and mathematical methods which are to be employed in the presentation. There follows a succinct chapter on the heat capacity of gases in which the author takes care to indicate the provisional nature of the theory of the specific heat of gases. The theory has complete quantitative success only in the case of hydrogen.

Before the treatment of chemical dissociation, and evaporation, the theory of the properties of crystals is given. The Born theory of the solid state is sketched and a generous amount of comparison between deduction and experiment is shown in the case of the heat capacity for solids. The equation of state for solids is derived on the basis of Born's "lattice theory."

The chapter on dissociation and evaporation, which will be of particular interest to chemists, is necessarily rather difficult reading. The treatment in its essential aspects is based on the 1920 work of Ehrenfest and Trkal with the restriction of "fully excited" or "completely unexcited" degrees of freedom removed. This chapter also includes the application of the theory to the vapor pressure of crystals.

The discussion of the relation of the statistical equilibrium theory to thermodynamics constitutes one of the most ably written sections of this noteworthy book. The proof that the laws of thermodynamics hold true for the assemblies is carried out by the use of analogies in pretty much the same manner as adopted by Gibbs in his "Mementary Principles of Statistical Mechanics." In the course of the discussion the fundamental basis of the statistical theory is critically reviewed, giving evidence of the painstaking thought that has been given to the difficult question of "weight" (*a priori* probability). The section of this chapter on entropy and Boltzmann's probability hypothesis is particularly well written.

Nernst's heat theorem and related topics, which can only be discussed in detail from the point of view of statistical mechanics, is sketched in an all too brief chapter. The theorem of Nernst, as originally derived, is wholly empirical and certainly "proves too much." The statement of the theorem by Lewis and Randall is drawn with the proper reservations. The author points out, however, that the extra hypothesis required to obtain the theorem (identity of weights of the lowest quantum states of all condensed systems) may not be true, as evidenced by the case of hydrogen.

The theory for imperfect gases represents a brave attempt but scarcely carries the problem beyond the old status. The limitations of the statistical method and the nature of the difficulties emerge clear-cut and definite, which in itself is a notable achievement in a field where an extraordinary amount of illusory theory has been written. When the need of considering the potential energy due to long range forces (case of ions in solution, for example) becomes important, difficulties arise due to the fact that the relative coordinates of the molecules or ions are insufficient to define the effects on the distribution expression. The problem has assumed much immediate importance since the papers of Debye and Hiickel on ionic solutions. Professor Fowler's able discussion of the character of the theoretical pitfalls inherent in the latter theory will be all too brief for those interested in the properties of solutions. The further discussion of dilute solutions and comparisons with experiment are given in a later chapter.

Considerable space is given to the theory as worked out for assemblies of atoms, ions and electrons, a condition of matter at very high temperatures. The dissociation theory given earlier is revised here in order to introduce terms representing essentially corrections for the potential due to electrostatic forces. The theory is also compelled to give attention to many details of atomic structure in order to develop a plausible set of rules for assigning "weights." With these details settled the analysis proceeds to develop the partition functions and finally encounters the same difficulties that beset Debye and Hiickel in the case of ionic solutions.

The development of the theory is of great importance and is carried as far as seems reasonably possible in view of the difficulties, mathematical and physical, inherent for the moment in the general situation. Applications of the equations (involving, as the author indicates frankly, certain speculative approximations) are made to the problems of stellar atmospheres and interiors. The theoretical side of the problem, it may be emphasized, is of pronounced interest in chemistry.

The general theory of molecular interaction or collision precedes a statement of the theory of gaseous chemical reaction velocity and radiative processes. The book ends with an excellent chapter on statistical mechanics based on the new quantum theory (wave mechanics).

The author makes gracious acknowledgment of the assistance of an unusually large number of very able collaborators who have contributed generously to the sustained excellence of this scholarly work. The book is really a masterpiece of critically presented scientific theory.

FREDERICK G. KEYES

Handbuch der biologischen Arbeitsmethoden. (Handbook of Biological Methods.) Edited by Professor Dr EMIL ABDERHALDEN. Section I. Chemical Methods, Part 2, 2d Half. Number 2. Chemische Reaktionen organischer Körper im ultravioletten Licht und im Licht der Sonne. (Chemical Reactions of Organic Compounds in Ultraviolet Light and in Sunlight.) By FRANZ BACHÉR, Rostock. Number 3. Sulfonieren. (Sulfonation.) By JOSEF HALBBRKANN and FRITZ FRETWURST, Hamburg. Biologisch wichtige Reaktionen und Reagenzien. By EDUARD STRAUSS and KARL KOULEN, Frankfort-on-Main. Number 4. Darstellung metallorganischer Verbindungen. (Preparation of Organometallic Compounds.) By EMIL KLARMANN, Bloomfield, New Jersey. Urban and Schwarzenberg, Friedrichstrasse 105B, Berlin N 24, Germany, 1928, 1929. No. 2, 630 pp. 25 figs. No. 3, 180 pp. No. 4, 159 pp. 3 figs. 17.5 × 25.5 cm. Price, No. 2, R. M. 32; No. 3, R. M. 10; No. 4, R. M. 8.

Abderhalden's Manual of Biological Methods deals with so many and such diverse topics, fundamental as well as applied, is so ambitious in aim and so comprehensive in scope, that it ranks as a new phenomenon in scientific publication. In view of the great diversity of subjects and the number of collaborators—six hundred—it was to be expected that the various installments would be very dissimilar in character. They are. And they are also very unequal in quality.

The three installments that are reviewed here all belong to the sub-section dealing with general chemical methods. The earliest one—number 254—is, doubtless, the most extensive treatise on the photochemistry of organic compounds that is available. Beginning with excellent chapters on "the photochemical reaction," "experimental procedures," "reaction participants," and the treatment of the products of the reaction," it passes on to a survey of the behavior of all the various classes of organic compounds that have been exposed to ultraviolet light or to direct sunlight and ends with a special section in which all known cases are tabulated with respect to: substances exposed, source of the light, nature of the process and character of the products. While the author here and there hints that a process is especially interesting to the biochemist, the text would probably be exactly the same if he had prepared it especially for the organic chemist.

This installment is invaluable to anyone who is interested in, or has occasion to examine, the photochemical behavior of an organic compound. The survey is complete, including references to the original literature; the material is well organized, and the judgments are critical. As a part of a larger volume the number has no separate index, but a very detailed table of contents in a great measure makes up for the lack of it.

The other two installments under review deal with similar subjects—the one the preparation of sulfonic and sulfuric acids, the other the preparation of organometallic compounds. These installments are very unequal in quality. The author of number 287 discusses the principles underlying the various methods of sulfonation, explains why methods that give admirable results with one class of substances must be modified before they are applicable to other closely related classes, and cites abundant examples for illustration. The author of number 294 contents himself with transcripts of the various directions that are to be found in the literature for preparing metal organic compounds. This method of treatment may be useful to an occasional biochemist to whom the sources are not accessible; the organic chemist will prefer the more critical and comprehensive treatises that are available.

E. P. KOHLER

Die Kiinstlichen Harze. (Artificigl Resins.) By JOHANNES SCHEIBER, Dr. Phil., Professor at the University of Leipzig, and KURT SÄNDIG, Dr. phil. Wissenschaftliche Verlagsgesellschaft m. b. H., Stiittgart, Germany, 1929. xv + **376 pp.** *29* **figs.** 16.5 X 25 cm. Price, unbound, M. 26; bound, M. 28.

This book is divided into three parts—general, theoretical and special. The general part contains a discussion of the nature of the resinous state and the molecular conditions responsible for its existence. The theoretical part contains a systematic discussion of the types of compounds and the kinds of reactions which lead to resin formation, together with a consideration of such information as is available concerning the structures of the molecules present in resins and the mechanisms by which they are formed. The third part is concerned with commercial methods of preparation, the properties, uses and the methods of testing the most important types of artificial resins. The authors have carefully surveyed the voluminous literature of this difficult subject up to the middle of 1928. The book is provided with subject, author and patent indexes.

This monograph will be indispensable to chemists who are directly interested in artificial resins, and the theoretical part especially will be useful to all chemists who are interested in the broader field of natural and synthetic polymers of high molecular weight.

WALLACE H. CAROTHERS

Praktikum der Färberei und Druckerei. By Dr. KURT BRASS, Professor at the Technical Nigh School of Prague. Second, revised edition. Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1929. viii + 104 pp. 5 figs. 14 × 21 cm. Price, R. M. 5.25.

This little work by Dr. Brass is an excellent example of what a laboratory manual should be. It presupposes a reasonably good knowledge of what dyestuffs are, and how divided into groups according to their generally most prominent chemical character, though it seems as though one who did not possess this preparatory knowledge to any great extent might work his way into the art of dyeing, so skilfully is the book constructed, and with such accommodation to the student "who did know, but has forgotten for the time being." It is not a mere set of directions for getting a piece of fabric or a lot of material dyed to a certain color, but a distinctively scientific introductory manual for the use of a serious student taking up training in dyeing operations for the first time.

Introductory sections cover such matters as the description of the different textile fibers, and their determination and distinction, the various classes of dyestuffs from both the practical and the structural side, the general methods of dyeing—preparation of the material, the solution, the bath, the apparatus, etc.—and pass into the main portion of the work—general methods of dyeing and practical examples in detail under each group of dyestuffs, with examples of after-treatment, when such exist. The final section deals in the same full way with the operations of printing. Appended to the section on dyeing is a chapter on the different standard methods for examining the fastness of the dyed material toward the various influences which affect it—light, washing, chlorine, etc.

The book is well printed, with arrangement and styles of type calculated to make instant reference to a particular point easy. It is properly bound instead of wired, and so will stay open and flat without one's having to bend and stretch the pages, or weight down each side of the open book as it lies upon the work-bench or desk. We wish very much that laboratory manuals of equally high excellence in all points were available for other branches of laboratory work, whether in German or English.

FREDERICK S. BEATTIE

Lehrbuch der Seifenfabrikation. (Textbook of Soap Manufacture.) BY DR. J. DAVIDSOHN. Gebrüder Borntraeger, W 35 Schöneberger Ufer 12 a, Berlin, Germany, 1928. xxiv + 731 pp. 105 figs. 16 × 24.5 cm. Price, unbound, M. 36.

This book is intended as a textbook of soap manufacture, addressed both to the academic chemist and to the practical soap chemist, showing the relation between theory and practice. It treats of the raw materials and methods of testing them (160 pages), plant commonly used (40 pages), theory (*23* pages), practice of soap boiling (**124** pages), manufacture of each of seven main classes of soap (**236** pages), methods of testing and analysis (*30* pages), and the by-products, lyes and glycerine (*22* pages), with a brief Appendix devoted to statistics and governmental regulations.

The book describes German manufacturing usage but contains little or nothing that is new or original. It does not, of course, attempt to compete with standard reference works such as Ubbelohde–Goldschmidt or Hefter, and it will not be widely used by American readers who have access to such existing books in English as those of Lewkowitsch–Warburton, Webb or Lamborn. On the theoretical side the book is decidedly lacking, the author ignoring the work of several of the leading schools in Germany, not to mention those of other countries. On the other hand, the author's practical experience as a consultant is reflected in numerous details he gives as to methods of testing and analysis.

JAMES W. MCBAIN

Kraemer's Scientific and Applied Pharmacognosy. Third edition, revised by E. N. Gathercoal, morphology; E. B. Fischer, constituents; L. K. Darbaker, literature and index; E. L. Newcomb, editor-in-chief, supervision. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1928. 405 illustrations. xxxvii + 893 pp. 15.5 × 23.5 cm. Price, $7.50.

The book is "intended for the use of students in pharmacy, as a handbook for the pharmacists and as a reference book for botanists, chemists, food and drug analysts, and pharmacologists."

Kraemer's undertaking was an ambitious attempt toward a comprehensive standard work for this country.

The revisers have evidently given most attention to the morphological descriptions and the book will continue to be very helpful in that respect.

Authoritative information on applied pharmacognosy, occurrence and especially on adulteration, requires such an intimate contact with the industry and thorough knowledge of present field and trade conditions that equal perfection is very difficult to attain.

Considerable further revision, addition and deletion are needed to bring the information given up to date. The same general suggestion is made in connection with statements referring to chemical composition, identification and evaluation, if the book is to serve as a "hand and reference book."

ARNO VIEHOEVER

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